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Trends, seasonal cycles and synoptic scale episodes of halocarbons observed in Ny-Ålesund, Spitsbergen

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Abstract

A study of the important gases in the air at the Ny-Ålesund measuring station at Svalbard is presented in this thesis. The monitoring station is located 474 m a.s.l. at Mt. Zeppelin, a mountain ridge with steep rocky slopes and glaciers on all sides.
SOGE is an integrated System for Observation of halogenated Greenhouse gases in Europe. A combination of observations and modeling is used to estimate regional emissions as well as global trends and impact on climate and the ozone layer. In situ observations at four background stations in Europe forms the back bone of SOGE.
A wide range of halogenated greenhouse gases are measured in situ at these four background measurement stations. The four stations are Mt. Zeppelin at Svalbard in arctic Norway, Mace Head in Ireland, Jungfraujoch in Switzerland and Mt.Cimone in Italy. Measurements are performed with high frequency by the use of automated gas chromatographs with mass spectrometry detectors.
Measurement data from the years 2001 - 2003 are analyzed in this thesis for trends and pollution events. Trends in background concentrations were also analyzed. Positive trends in the background concentrations were observed for substances which are used as CFC-substitutes (hydrofluorcarbons, hydroclorofluorcarbons). Background concentrations in the HFCs at Ny-Ålesund increased from January 2001 until December 2003 as follows: HFC-125 from 1.8 to 3.5 ppt, HFC-134a from 21 to 31 ppt, and HFC-152a from 2.8 to 4.3 ppt. All peak concentrations of the measured gases were significantly lower at Ny-Ålesund than other sites, due to the stations remote location. The peak events were analyzed separated to see if there were any trends in the pollution pattern. Events of polluted air masses were studied in combination with air mass trajectories from European, Atlantic, Russian and North American sectors to allocate specific source regions.

Contents

Chapter 1

Introduction

1.1 Introduction

The solar energy which reaches the ground heats the Earth and is transformed into infrared rays. Like the glass panes of a greenhouse - hence the name given to this mechanism - the gases in the atmosphere trap parts of these rays and they in turn heat up the atmosphere. Thus, in terms of power, the Earth receives on average a little more than 240 watts/m^2. Without the greenhouse effect, the average temperature on Earth would be -18°C and there would be very little water in liquid form. Therefore, this effect is beneficial, since it enables our planet to maintain an average temperature of +15°C. The atmospheric gases contributing to this heating are called greenhouse gases. Some of these gases have large natural sources, like carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). They have sustained a stable atmospheric abundance for the centuries prior to the industrial revolution. Emissions due to human activities have caused large increases in their concentration levels over the last century, adding to radiative forcing.

The synthetic man made greenhouse gases, such as CFCs, HCFCs and HFCs did not exist in the atmosphere before the 20th century. Although these gases have much lower concentration levels than several natural gases, they are strong infrared absorbers, and current concerns about the atmospheric levels of CFCs, HCFCs and HFCs in the atmosphere are based on their effect on the stratospheric ozone layer [Molina and Rowland, 1974] and on surface climate [IPCC 1996].

Stratospheric ozone depletion is known to be caused by chlorine originating from CFCs and related chemicals as well as by bromine from industrially produced halons. It occurs most naturally in connection with the formation of cold, stratospheric clouds. The depletion is highly dependent on the meteorological circulation pattern, particularly with the formation of isolated air packets characterized by the potential vorticity in the upper atmosphere. Unlike in the Antarctic, the Arctics strong meridional circulation extends into and even across the polar cap. It is possible to observe both the effect of isolated anthropogenic releases from Europe, Asia and North America as well as the slow changes of global atmospheric composition.

The gases have a wide variety of applications such as refrigeration, foam blowing and fire extinction [Midgley and McMulloc, 1999]. Regarding their environmental impact, these substances can further be divided into two main groups. The first group consist of halocarbons responsible for the depletion of stratospheric ozone, i.e. CFCs, HCFCs and long lived chlorinated solvents. The substances are regulated in the Montreal Protocol and are due to be phased out worldwide. The second group combines halocarbons with fluorine as the only halogen i.e. HFCs. These substances do not have a direct effect on stratospheric ozone, but contribute to global warming and where therefore included into the Kyoto Protocol.

The lifetimes, atmospheric trends and emissions of compounds are undergoing continuous review processes. While the CFCs are about to level out or in case of CFC-11 decreasing, the HCFCs are showing moderate increase rates, while the HFC concentrations in the atmosphere are still showing substantial yearly increase. The averaged seasonal cycle for some of the measured components are clearly showing a winter/spring maximum and a summer/fall minimum associated with the compounds predominant removal process in the atmosphere trough its reaction with the OH radical. Shifts in the wind pattern and biological sources in the ocean do also contribute to the averaged seasonal cycle.

The concentration of atmospheric trace gases in the Arctic is highly influenced by long-range transport from mid-latitude source regions [Barrie and Hoff, 1985]. In particular, the meteorological conditions during winter and early spring are favorable for transport of air mases from mid-latitude industrialized areas into the Arctic. Most of the air sampled at Ny-Ålesund is clean Arctic air. Over a suitably long period (i.e. year or season) the station is presumed to have adequately sampled the distribution of lower tropospheric air masses characteristic of the Arctic region. This sampling would be characterized by both positive and negative fluctuations about the (e.g monthly or seasonal) mean with periods associated with synoptic scale meteorological events. A minimum of several measurements per day is required to adequately resolve the typically 1-to-3 day pollution events. Due to Mt.Zeppelins remote location, the studies of events are limited to a few case studies.

Chapter 2

Station

2.1 The Zeppelin station

Figure 2.1: *The Zeppelin station*

The monitoring station is located on the Zeppelin Mountain, close to Ny-Ålesund at Svalbard. At 79°N the station is placed in an undisturbed arctic environment, away from major pollution sources. Situated 474 meters a.s.l. and most of the time above the inversion layer, there is minimal influence from local pollution sources in the nearby small community of Ny-Ålesund.

The station was officially opened in 1990. After 10 years of use, the original building was replaced by a new modern station that was opened in May 2000. The new monitoring station was realized by funds from the Norwegian Ministry of Environment and the Wallenberg Institution via Stockholm University (SU).

The unique location of the station makes it an ideal platform for the monitoring of global atmospheric change. The measurement activities at the Zeppelin station do also contribute to a number of other global, regional and national monitoring networks.

The Siberian High is an intense, cold anticyclone that forms over eastern Siberia in winter. Prevailing from late November to early March, it is associated with frequent cold air from north to Svalbard. The dominant wind direction across the the islands is from SSE toward NNW. Even during the summer, wind from north-west and north may bring cold polar air masses to the Zeppelin station within few hours.

Chapter 3

Data and method

3.1 Observations

3.1.1 Compounds

Chemical formulae	Industrial name	Atmospheric lifetime
$\mathbf{CCl_3F}$	CFC-11	52
$\mathbf{CCl_2FCClF_2}$	CFC-113	85
$\mathbf{CClF_2CF_3}$	CFC-115	1700
$\mathbf{CHClF_2}$	HCFC-22	13.3
$\mathbf{CHCl_2CF_3}$	HCFC-123	1.4
$\mathbf{CHClFCF_3}$	HCFC-124	5.5
$\mathbf{CH_3CCl_2F}$	HCFC-141b	9.4
$\mathbf{CH_3CClF_2}$	HCFC-142b	19.5
$\mathbf{CHF_2CF_3}$	HFC-125	33
$\mathbf{CH_2FCF_3}$	HFC-134a	15
$\mathbf{CH_3CHF_2}$	HFC-152a	1.5
$\mathbf{CBrClF_2}$	H-1211	20
$\mathbf{CBrF_3}$	H-1301	65
$\mathbf{CH_3Cl}$	Methyl Chloride	1.3
$\mathbf{CH_3Br}$	Methyl Bromide	0.7
$\mathbf{CH_3I}$	Methyl Iodide	0.02
$\mathbf{CH_2Cl_2}$	Methylene Dichloride	0.5
$\mathbf{CH_2ClCH_2Cl}$	Dichloroethene, DCE	0.19
$\mathbf{CH_3CCl_3}$	Methyl Chloroform, MC	6
$\mathbf{CCl_4}$	Carbon Tetrachloride, CT	24

Table 3.1: *Halocarbons used in this document and their atmospheric lifetime in years.*

HFCs and HCFCs are used as interim substitutes for CFCs, halons and chlorinated solvents.

CFC-11 was introduced in the 1930s as a refrigerant. Production and emissions first remained low but, increased rapidly in the 1960s with the spread of refrigeration in the developed world and as new uses, such as aerosol

spray cans, were developed. It was later principally used as a blowing agent for foams and packaging materials and as a refrigerant in large commercial chillers. Sales have been declining since 1988, with production following roughly the same trend. The replacement of CFC-11 has been mostly by HCFC-141b. The atmospheric lifetime is 52 years.

CFC-113 is principally used as a solvent, and it volatilizes easily. Emissions of CFC-113 have been declining rapidly since 1988. Recycling and treatment of CFC-113 have also declined in recent years, indicating that the gas is being phased out in favor of alternatives. The atmospheric lifetime of CFC-11 is 82 years.

CFC-115 is used primarily as a blending agent for refrigerants. The last U.S. sale was reported in 1986. No recycling or disposal in developing countries was reported in 1993. The lifetime of CFC-115 is as long as 1700 years, and the gas is removed from the atmosphere very slowly.

Throughout the 1970s and early 1980s, the CFC releases continued to grow, and they were transported to the stratosphere and decomposed there to release chlorine or bromine. CFC-113, CFC-114, CFC-115, H-1211, H-1301, carbon tetrachloride and methyl chloroform all showed growth. [P.M. Midgley and A. McCulloch, 1999]

HCFC-22 is the most commonly used refrigerant for home air conditioning systems. In 1994 it was the most widely available and least expensive potential substitute for CFCs.

HCFC-123 is per 1994 a potential replacement for CFC-11 in refrigeration applications. HCFC-123 is also used as foaming agent and cleaning agent. The atmospheric lifetime is 1.4 years.

HCFC-124 is a potential replacement for CFC-12. HCFC-124 is used as refrigerant, fire extinguishing agent and as alternative for CFC-114.

HCFC-141b may be used as a solvent and in blends to CFC-11 blowing agents. HCFC 141b can be used as foaming agent, and cleaning agent as alternative for CFC-11 and CFC-113.

HCFC-142b is a CFC replacement, and is mainly used as refrigerant under high temperature and component of blend refrigerant.

All the HCFCs have atmospheric lifetime shorter than 20 years.

HFC-125 is a CFC and HCFC replacement. HFC-125 is used as refrigerant, fire extinguishing agent and alternative for CFC-112, HCFC-22, Halon-1211 and Halon-1301. The current tropospheric background is relatively low, but the lifetime is 33 years, and the gas is removed from the atmosphere very slowly.

HFC-134a is an important replacement for CFCs in automotive air conditioners. HFC-134a replaced CFC-12 in virtually all vehicle air conditioners produced after 1993/94. [Gentner, 1998] The gas is, together with HFC-125, a replacement for HCFC-22 in new or existing air-conditioning equipment and heat pumps. HFC-134a is also used extensively as a refrigerant agent, and to a lesser degree as a foam-blowing agent. The atmospheric lifetime is 15 years.

HFC-152a can be used as a blowing agent and as an ingredient in refrigerant blends. It is currently emitted at a rate that is higher than the rate of removal from the atmosphere and the background concentration is increasing. The gas is a substitute of HCFC-141b. HFC-152a is also used as a temperature sensing agent, as alternative for CFC-12 as refrigerant and as aerosol propellant. Atmospheric lifetime is estimated to be 1.5 years.

Because HFCs are composed of only carbon, hydrogen and fluorine, they do not destroy ozone.

H-1211 and **H-1301** are used as fire suppressants, and H-1301 also receives minor use as a cold-temperature refrigerant. They are destructive to stratospheric ozone, and consequently production is decreasing as per agreements in the Montreal Protocol.

Methyl Chloride, CH_3Cl, is the most abundant halocarbon in the atmosphere. It is derived largely from natural sources, mostly biomass burning and the oceans.

Methyl Bromide, CH_3Br, is currently used as a soil and crop fumigant. Automobile emissions from burning of leaded gasoline are also anthropogenic sources of CH_3Br. Unlike CFCs and halons, there are large natural sources and tropospheric sinks for Methyl Bromide. Since bromine is far more effective at destroying ozone than chlorine (by a factor of 30-60), even a small amount of stratospheric bromine can be important. Current international regulations call for a cap on Methyl Bromide production, while US law calls for it to be phased out. Methyl Bromide used as a fumigant in countries not defined by the Montreal Protocol was scheduled to have begun decreasing after 1998. Production of CH_3Br in the developed countries was reduced from 1991.

Methyl Iodide, CH_3I, is mainly emitted to the atmosphere from the oceans, and it is of interest in the atmosphere as a tracer of marine convection. It is also emitted from biomass burning and wood fuel. CH_3I is of interest in the upper troposphere as a source of iodine radicals for potential ozone destruction. CH_3I is the leading candidate to replace CH_3Br as a soil fumigant. [Waggoner et al., 2000]. Methyl Iodine is scheduled to be phased out in use as an agricultural chemical in the developed countries by the year 2005.

Methylene Dichloride, CH_2Cl_2, does not occur naturally in the environment. Methylene Dichloride is used as an industrial solvent and as a paint stripper. It may also be found in some aerosol and pesticide products and it is used in the manufacture of photographic film. Methylene Dichloride has been identified as a substitute for flexible polyurethane foam, but it is more toxic than HCFC substitutes. Regulators, such as the U.S. Environmental Protection Agency (EPA), have stated that Methylene Chloride is not expected to be a significant substitute for CFC-11.

Dichloroethylene, DCE, does not occur naturally in the environment. It is produced commercially by thermal decomposition of Methyl Chloroform. DCE is also used as a captive intermediate in the production of hydrochlorofluorocarbons (HCFC-141b and HCFC-142b), and in the production of homo-, co-, and terpolymers (latex and resin). The polymers are used in a variety of consumer products, including food packaging, textiles and outdoor furniture. Dichloroethylene is frequently found at hazardous waste sites.

Carbon Tetrachloride, CT, was originally used as a household cleanser and dry-cleaning solvent. Carbon Tetrachloride is also used as feedstock for the production of CFC-11. Its production was phased out in 1996 in Europe and in the US.

Methyl Chloroform, MC,: industrial production and release to the atmosphere of Methyl Chloroform declined dramatically in the 1990s [McCulloch and Midgley, 2001; UNEP, 2002]. In the developed countries it was phased out in 1996. Declines in emission closely followed declines in production because Methyl Chloroform was used predominantly in applications where releases occurred soon after sales. Reports have suggested that small amounts of Methyl Chloroform are emitted from biomass burning.

Compound	2001 mean	2002 mean	2003 mean
CFC-11	262	266	263
CFC-113	81.3	82.3	82.9
CFC-115	8.24	8.57	8.57
HCFC-22	162	167	170
HCFC-123	1.18	1.07	1.10
HCFC-124	1.54	1.69	1.78
HCFC-141b	17.0	19.0	19.1
HCFC-142b	14.9	15.8	16.4
HFC-125	1.85	2.58	3.47
HFC-134a	21.1	26.4	30.7
HFC-152a	2.78	3.41	4.25
H-1211	4.43	4.52	4.57
H-1301	2.97	3.17	3.29
Methyl chloride	499	518	534
Methyl bromide	8.63	9.28	8.51
Methyl iodide	0.67	0.85	0.66
Methylene chloride	30.2	29.8	32.7
DCE	81.3	82.7	82.9
MC	35.0	32.4	28.2
CT	93.9	93.0	95.1

Table 3.2: *Yearly mean concentration levels of climate gases at the Zeppelin station. All concentrations in ppt.*

3.1.2 Sampling frequency

The instrument at Mt.Zeppelin provide a sample every 4. hour. The atmospheric lifetimes of the components evaluated in this thesis are on a longer time scale than days/weeks. The day/night chemistry can, in our case, normally be neglected, so that the daily means are calculated and used. A file containing trajectory information about the sectors is in 6 hr resolution.

3.1.3 Instrument

The instrument is a fully automated adsorption/desorption sampling device (ADS) coupled with an automatic gas chromatograph with a mass spectrometric detector (GC-MS). The system provides 6 air samples during 24 hours. The instrument is the same instrument as the ones located at the SOGE stations Mace Head and Jungfraujoch and all the five AGAGE (Advanced Global Atmospheric Gases Experiment) sites. The four sites within the SOGE project are using calibration tanks, which are pressurized simultaneously at Mace Head and then calibrated to AGAGE scale. The instrument currently monitors more than 20 compounds, including CFCs, HFCs, HCFCs, halons and a range of other halogenated species.

There are about 4 to 6 visits from NILU each year for major maintenance work on the instrument. All data are transferred to NILU on a daily basis.

All data are processed by software, which is common for all AGAGE and SOGE stations.

3.1.4 Available data record

In this work with the SOGE data, the focus will be on years 2001 - 2003. Instrumental problems in May/June 2001 and in April/May 2002 resulted in periods of data loss. There have been short interruptions in the measurements due to periodical maintenance, but overall data coverage is considered very good for 2001 and 2002. For 2003 we must mention that hard disc crash in January, lack of calibration gas in beginning of April, bad instrument performance in July - September due to leak problems and broken turbo pump in the MS and broken water trap in November, resulted in data losses in these periods. In consideration of these periods of data losses, the overall data coverage is considered to be good for the year 2003. Losses of data due to mechanical failure of the monitoring equipment or poor quality data, which has to be removed, will also adversely affect the accuracy of the long term trend derivations. Future continuation of in situ GC-MS observations and subsequent quality control filtering should enable more reliable trend estimations.

3.2 Sorting the data

3.2.1 Determination of background data

Based on the daily mean concentrations, an algorithm is selected to find the values assumed as clean background air. If at least 75% of the trajectories within +/- 12 h of the sampling day are coming from a so called clean sector, defined in section 3.3.1, one can assume the air for that specific day to be non polluted. The remaining 25% of the trajectories from either European, Russian or North-American sector are removed before calculating the background. For HFC-134a and HFC-152a, figure 3.1 and figure 3.2, and for the other measured components not shown here, we find that most of the spikes, i.e. assumed polluted events, are removed during the filtering. One can assume that the chosen filter is a good method for finding mean background concentrations for further work. For both HFC-134a and HFC-152a we can see that peak values are removed in September 2001, in May 2002 and in December 2002. We will later see that there are a few more events worth further investigation as well.
Background data points selected with the method used in this paper are about 60% of the total data set.
There are more methods for finding the best estimate continuous baseline, based on daily means. Those methods are briefly shown in section 3.2.2.

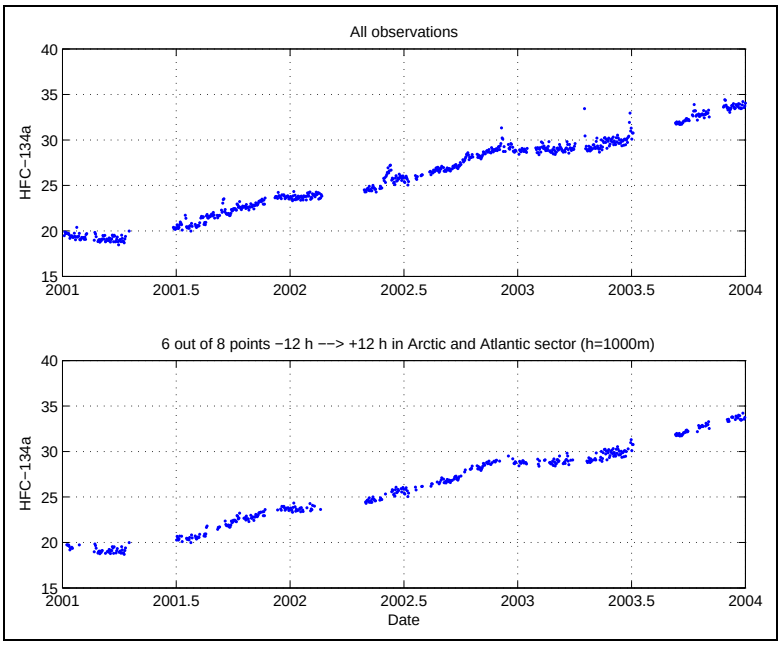


Figure 3.1: *Finding the mean background data, HFC-134a. Upper panel shows all daily observations, lower panel shows data selected for background concentration calculations.*

3.2.2 Curve fitting

Long term monotonic trends and seasonal and interannual oscillations are studied in this thesis. The distinct annual cycles in concentrations can be explained at least qualitatively in terms of distances from sources (largely northern latitude), intensity and seasonality of the global circulation. For some components, like Methyl Chloroform and other components with atmospheric lifetime shorter than a few years, the seasonal cycle in their reaction with OH is also used to explain the annual cycles.
First we fit our data to a set of harmonic functions.

$$f(t) = a + bt + c_1 cos(2\pi t) + s_1 sin(2\pi t) + c_2 cos(4\pi t) + s_2 sin(4\pi t) + c_3 cos(6\pi t) + s_3 sin(6\pi t) + c_4 cos(8\pi t) + s_4 sin(8\pi t) \quad (3.1)$$

The coefficient a defines the average mole fraction and b defines the trend in the mole fraction. The c's and s's define the annual cycle in mole fractions. t is the time in years, measured from the beginning of the 2N-year interval of interest. The periodic and cyclic pattern fits well with the gases that have a stable year to year trend, like HFC-134a, showed in figure 3.3 (upper panel), HFC-152a, showed in figure 3.5 (upper panel), and CH_3Cl, showed in figure 3.6 (upper panel).
The blue background line in the figures is based upon the same data points as the earlier suggested background data. The line is mainly located at or below the daily means, which indicates that most of the selected data points can be classified as clean background air.

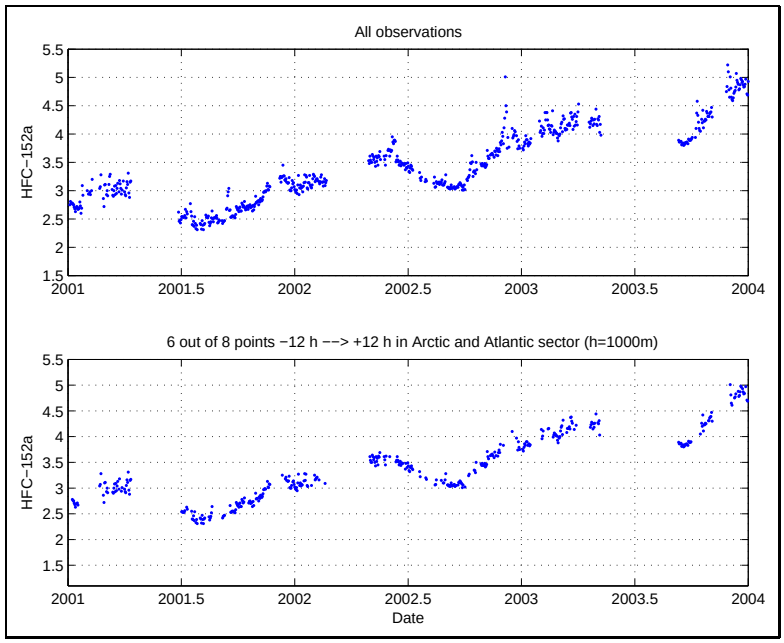


Figure 3.2: *Finding the mean background data, HFC-152a. Upper panel shows all daily observations, lower panel shows data selected for background concentration calculations.*

The compounds that have a strong seasonal variation in the concentration, due to the reaction with OH radicals in the atmosphere, will fit the harmonic curve better than the other compounds discussed in this paper.
For the gases that have a sudden change in the growth rate, described by a step function, the harmonic function with its typically cyclic period does not fit the data very well. In the upper panel in figure 3.4 we see an example of a gas, HFCF-141b, that will not fit the harmonic function. HCFC-141b have a sudden increase in the concentration in 2001, while the concentration level is flatting out in 2002 and 2003. The harmonic function does not reproduce this change in the pattern.

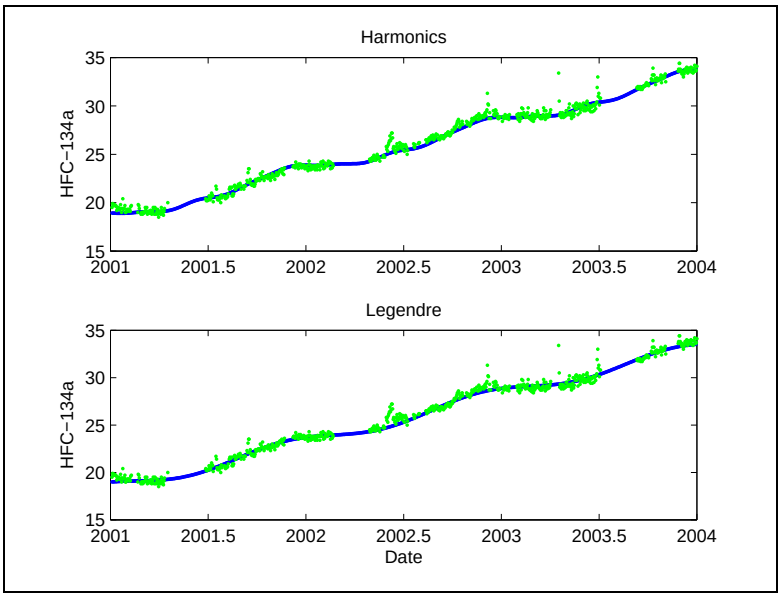


Figure 3.3: *Upper panel shows the background data plotted as a harmonic function (blue line) overloaded the daily means for HFC-134a. Lower panel shows the background data as a function of Legendre polynomials (blue line) overloaded the daily means for HFC-134a.*

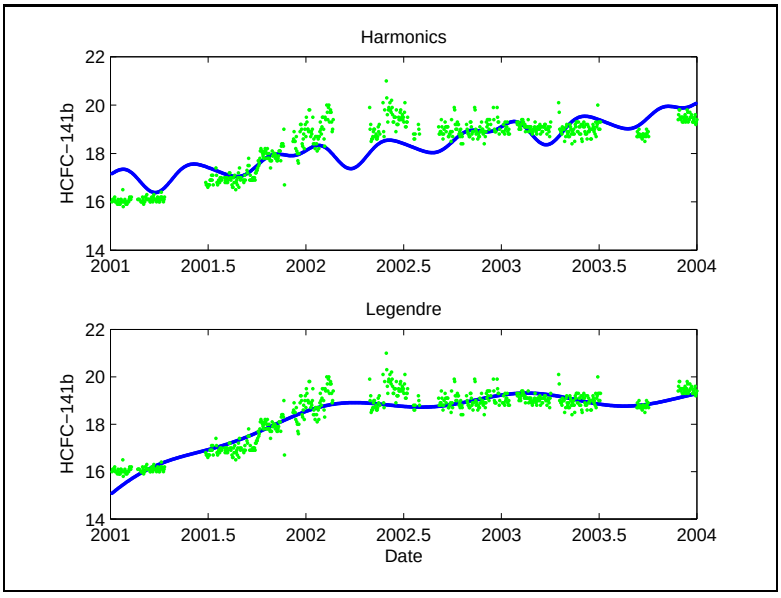


Figure 3.4: *Upper panel shows the background data plotted as a harmonic function overloaded the daily means for HCFC-141b. Lower panel shows the background data as a function of Legendre polynomials overloaded the daily means for HCFC-141b.*

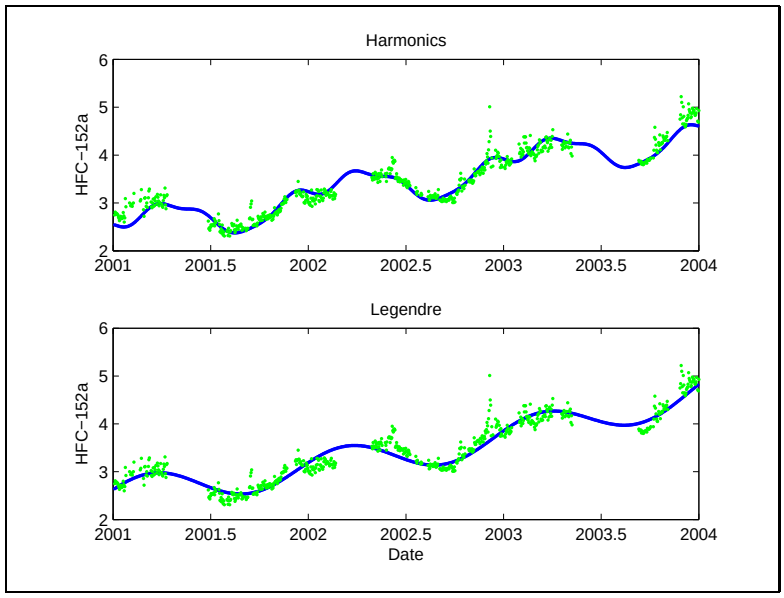


Figure 3.5: *Upper panel shows the background data plotted as a harmonic function (blue line) overloaded the daily means for HFC-152a. Lower panel shows the background data as a function of Legendre polynomials (blue line) overloaded the daily means for HFC-134a.*

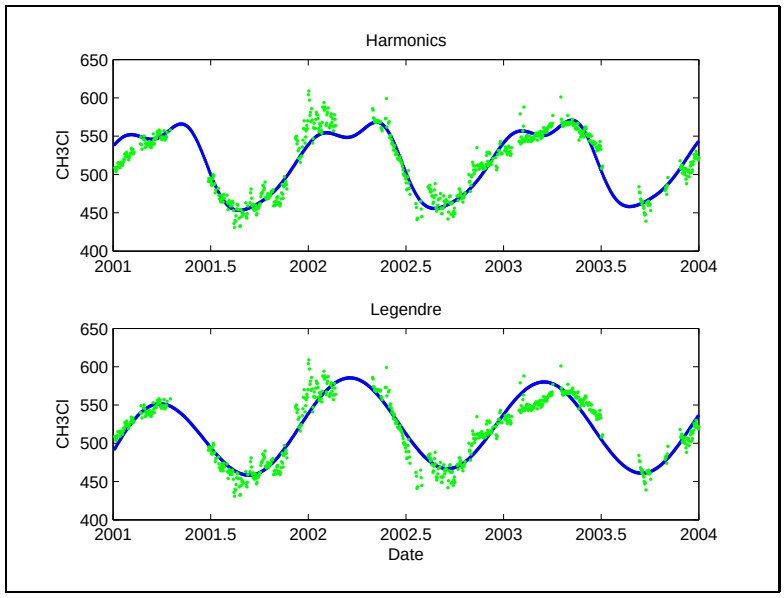


Figure 3.6: *Upper panel shows the background data plotted as a harmonic function overloaded the daily means for CH_3Cl. Lower panel shows the background data as a function of Legendre polynomials overloaded the daily means for HCFC-141b.*

A close look at the observations reveals that the fluctuations on a scale less than one year are less pronounced than the yearly ones. On the other hand, variations on longer timescales are important. To take this into account, we introduce Legendre polynominals.

$$f(t) = a + bNP_1(t/N-1) + (1/3)dN^2P_2(t/N-1) + (1/8)eN^3P_3(t/N-1) + c_1cos(2\pi t) + s_1sin(2\pi t) \quad (3.2)$$

The observed f can be expressed as functions of time measured from the 2N-year interval of interest. The coefficient a defines the average mole fraction, b defines the trend in the mole fraction and d defines the acceleration in the trend. The c and s define the annual cycle in mole fractions. N is the mid point of the period of investigation. The polynomial P_3 (with coefficient e) is small, but added to better fit the full data set. The detrending of the baseline by harmonics allows the generation of the seasonal cycle of each measured compound per year of data, which is then aggregated to develop an annual averaged seasonal cycle for each compound. The cycles for the long lived components result from a combination of seasonal cycles (if any) in their release (mainly from NH mid-latitudes) and seasonal cycles in their transport. For the components with shorter atmospheric lifetime, e.g. weeks/months, the annual cycles in their atmospheric destruction by OH (summer maximum and winter minimum) are superimposed on their source induced and transport induced cycles. The two latter are apparently approximately in phase, and both appear to contribute to the observed behavior. This presumes no strong seasonality in the emissions.

Examples of use of the Legendre polynomial fit function in combination with harmonic functions are showed in the lower panel in figure 3.3 - 3.6. It is easily seen that this method fits both regular and irregular trends in the different gases.

3.3 Trajectories and meteorological data

3.3.1 Sectors

Due to Mt.Zeppelins remote location, the amplitudes of polluted events are small and the episodes are rare. To obtain more specific information of the seen episodes, the incoming trajectories are studied and divided into sectors. 10 days backward trajectories from the European Center for Medium-range Weather Forecasts (ECMWF) have been used to investigate the major transport pathways into the region. The spatial resolution is T106, which correspond to a latitude/longitude resolution of 1.125 x 1.125, the temporal resolution is 6 hours and 60 levels are available in the vertical direction. The data sets are so-called analyzes which is a combination of observations and numerical calculations. Measurements from satellites, radio sondes, bouys, weather stations, etc. are assimilated into a meteorological model, that produce an estimate of the state of the atmosphere at a given time. [A. Stohl, 1995, S. Solberg, 2004]

Compound	2001-2003 mean	b,trend	d,change in trend	s	c
CFC-11	264	3.46	-2.83	2.82	-0.02
CFC-113	82.0	1.19	-0.19	0.33	-0.25
CFC-115	8.37	0.24	-0.05	0	0
HCFC-22	167	5.77	-0.57	-0.02	0.89
HCFC-123	1.12	-0.05	0.01	0.03	-0.04
HCFC-124	1.67	0.14	-0.02	0.02	0.02
HCFC-141b	18.2	1.93	-0.93	0.19	0.19
HCFC-142b	15.6	0.82	-0.10	0.12	0.05
HFC-125	2.60	0.95	-0.90	0.02	0.18
HFC-134a	26.1	4.99	0.17	-0.4	0.5
HFC-152a	3.39	0.59	0.03	0.33	0.12
H-1211	4.47	0.09	-0.01	0	0
H-1301	3.14	0.20	0.08	-0.02	0
CH_3Cl	515	20.9	-17.0	56.8	14.3
CH_3Br	8.85	0.40	-0.82	0.46	0.38
CH_3I	0.66	0.05	0.15	-0.08	-0.27
CH_2Cl_2	30.5	-0.15	1.15	6.12	1.89
DCE	0.66	0.12	0.04	0.25	0.18
MC	34.0	-3.42	1.00	-0.39	-0.22
CT	93.9	1.36	-1.10	0.41	-2.75

Table 3.3: *Mean mole fractions (a), Trends (b), Curvatures (d), and Seasonal cycles (c and s) for the compounds in SOGE at Mt. Zeppelin. Observations for the period 2001 - 2003 using equation (3.2)*

Air mass trajectories with all trajectory points north of 65°N were classified as Arctic. 58% of the trajectories are 'Arctic' trajectories.

If the trajectory was non-Arctic, the number of trajectory points south of 60°N was counted and:

If at least 50% of the trajectory points were between 70°W and 180°W the sector were classified as North American. 2% of the trajectories are 'North American' trajectories.

Air mass trajectories with all trajectory points between 10°W and 70°W the sector were classified as Atlantic. 7% of the trajectories are 'Atlantic' trajectories.

When at least 50% of the trajectory points were between 10°W and 30°E, the sector were classified as European. 7% of the trajectories are 'European' trajectories.

For air mass trajectories with all points between 30°E and 180°E the sector were classified as Russian sector. 6% of the trajectories are 'Russian'

trajectories.

20% of the trajectories do not come from any distinct sector and are therefore classified as 'undefined'.

The Arctic and the Atlantic sector are assumed to have minimal influence of pollution. There are no industrial sources in these areas, and one can say that the air is 'clean'. Background values are defined from those 'clean air' areas with 6 out of 8 trajectories (sampling day +/- 12 h) within sector, as described in section 3.2.1.
We find that most of the polluted episodes are following trajectories from European and/or from Russian sector.

Chapter 4

Long term variations

The monitoring at the Zeppelin Mountain Station in 2001 - 2003 revealed that the upward trend of most greenhouse gases in the atmosphere continued. The highest percent increase was the 25% rise of the concentrations of HFC-125 and HFC-134a which is even more than the 20% rise measured the year before. [SFT-report, 2003] This rise is probably a consequence of the phasing-out of CFCs controlled by the Montreal Protocol, as HFCs have been introduced as substitutes for HCFCs and CFCs. Even though global emissions of CFCs have been reduced considerably over the last few years, only small reductions in the concentrations of CFCs have been registered so far and some CFC species are even still growing in concentration. This is likely due to the fact that these gases have very long lifetimes in the atmosphere.

The HCFCs have shorter lifetimes than CFCs, due to the hydrogen bond, which is a reactant in dissociation, and thus have a more seasonally trend.

As the atmospheric mixing ratios of CFCs and chlorinated solvents decline, as we shall see later, the CFC replacement compounds, HCFCs, are contributing relatively more chlorine to the global chlorine burden.

The 3-year records of CFCs, HCFCs, HFCs and some other compounds' data at Mt.Zeppelin are shown in figure 4.1 - 4.4. All observations, including elevated events or 'polluted episodes' are a feature of the data superimposed on a seasonally varying monthly baseline. The monthly means in this baseline are calculated from the 'clean' daily means described in section 3.2.1. Some of the components contain more elevated plumes than other components, consistent with the diverse nature of the biological sources and the localized, urban sources of the different compounds.

The HFCs were introduced as CFC replacements in the early 1980s, and their individually concentrations were more than doubled in the 3 years of investigation.

All major CFCs are now in decline. The CFCs are the major source of chlorine to the stratosphere; in 2003 they accounted for 63% of the total chlorine burden.

Updated ground-based measurements of chlorofluorocarbons (CFCs) show that surface mixing ratios of CFC-113 peaked around 1996 and have been decreasing slowly thereafter. The decrease noted for CFC-11 mixing ratios in 1996 has continued [Montzka et al., 1999; Prinn et al., 2000].

In 2001 - 2003, the tropospheric mean mixing ratio of CFC-11 at Mt.Zeppelin is about 264 ppt. For the period, the trend in CFC-11 seems to be increasing with a growth rate about 3.46 ppt/year, but the increase in the trend is negative, -2.83 ppt/year^2. The mixing ratio of CFC-11 was at its highest in spring 2002 and decreased in late 2002 and 2003.

The mixing ratio of CFC-113 is about 82 ppt in the period of investigation. The growth rate for CFC-113 in 2001 - 2003 is slightly positive, but the trend in the growth rate is negative, 1.19 ppt/year and -0.19 ppt/year^2 respectively.

CFC-115, figure 4.1f), seems to have a higher growth rate in the first part of 2002 than in 2001, with mixing ratio increasing from 8.2 ppt to 8.6 ppt. The mean mole fraction in 2001 - 2003 is 8.37 ppt. The total trend has an increase, 0.24 ppt/year, but the increase is declining at a rate of -0.05 ppt/year^2.

Updated measurements of global hydrochlorofluorocarbons (HCFCs) indicate that global mixing ratios of the three most abundant HCFCs continue to increase in the atmosphere, owing to sustained emissions [Montzka and Fraser, 2002]. HCFCs make up about 6% of the total 2003 chlorine burden in the atmosphere.

Measurements suggest mixing ratio at Mt.Zeppelin for HCFC-22 of 167 ppt in 2001 - 2003, and a growth rate from 2001 to 2003 at 5.77 ppt/year. The growth rate is declining at a rate of -0.57 ppt/year^2, indicating that the growth trend is flatting out. The global rate of increase of HCFC-22 has remained fairly constant since 1992, [O'Doherty et al. 2004].

From figure 4.2b) we see that HCFC-123 is the only of the HCFCs that seems to be decreasing. We can see a slightly lower concentration value from year to year, with a decrease of 7% in 2001 - 2003, from 1.18 ppt to 1.10 ppt. The average mixing ratio for the 3 years of interest is 1.12 ppt. The general trend is negative and constant, -0.05 ppt/year.

HCFC-124, shown in figure 4.2c), is the compound that has the highest rate of increase of all the HCFCs, with a growth rate of 16% for 2001 - 2003. The yearly mean concentration at Mt.Zeppelin increased from 1.54 ppt in 2001 to 1.78 ppt in 2003. There is a lot of noise in the data for this component, which might contribute to uncertain calculations, but the general trend is 0.14 ppt and slightly decreasing.

The global emissions of HCFC-141b were strongly reduced from 2000 to 2003, in line with the results in Figure 4.2d). Measurements at Mt.Zeppelin show that the mean mixing ratio of HCFC-141b rose from about 17 ppt in 2001 to nearly 19 ppt in 2002, compared to a rise of only 0.1 ppt to 19.1 ppt in 2003. The growth rate from 2001 to 2003 is 1.93 ppt/year and decreasing at a rate of -0.93 ppt/year^2.

The rate of increase seen for HCFC-141b may also be shown for HCFC-142b. In 2001 the yearly growth rate was exponentially, and it slowed significantly during 2002 - 2003. Mean mixing ratio of HCFC-142b in 2001 - 2003 is 15.6 ppt. With a current, slightly decreasing, growth rate of 0.8 ppt/year for 2001 - 2003 one can assume the concentration to be stable at the same level for some years from now.

Figure 4.1a), b) and c) show that the rate of growth in the HFC-125, HFC-134a and HFC-152a baselines have increased over the period of SOGE observations (2001 - 2003). All HFCs seems to have a significantly greater growth rate in end 2002 than other years. All HFC mixing ratios are at their highest at the end of the 2001 - 2003 period.

The mean mole fraction for HFC-125 in 2001 - 2003 is 2.60 ppt. The growth rate from 2001 to 2003 is 0.95 ppt/year, and slightly declining.

For the 2001 - 2003 period, the trend in HFC-134a seems is increasing at a rate of 4.99 ppt/year, and the increase in the trend is positive, 0.17 ppt/year^2. The mean mixing ratio of HFC-134a were 26 ppt, and at its highest in the end of the measuring period.

Measurements suggest a mean mixing ratio at Mt.Zeppelin for HFC-152a of 3.4 ppt in 2001 - 2003, and a nearly constant growth rate from 2001 to 2003 at 0.59 ppt/year.

Although the phaseout was imposed on halon production in developed countries earlier than for all other halocarbons, mixing ratios of both Halon-1211 and Halon-1301 continued to increase at Mt.Zeppelin in 2001 - 2003.

Mixing ratios of H-1211 and H-1301 increased less rapidly in 2002 - 2003 than in earlier years. Due to the short period of investigation in this paper, this is not seen in figure 4.3a) and 4.3b). The mean mixing ratio for the 2001 - 2003 period is 4.47 ppt for H-1211 and 3.14 ppt for H-1301. The total growth rate for the period of investigation is 0.09 ppt/year and steady for H-1211 and 0.20 ppt/year and decreasing at a rate of -0.1 ppt/year^2 for H-1301.

From 2001 to 2003 atmospheric Brom (Br) from the sum of these halons increased at a mean rate of 0.08 ppt/year. The greatest part of this growth comes from the increase in H-1211. The growth rate of 0.09 ppt/year is lower than observed in the mid-1990s when Br from these gases increased at a rate between 0.2 and 0.3 ppt/year. The global mean rate of increase for

Halon-1211 during 2002 - 2003 was 0.04 ppt/year. [Madronich et al., 1999; Montzka et al., 2003b]

The fact that halon production in both developed and developing countries is now limited [WMO, 2003], suggest that accumulation rates for halons will continue to decrease in the years to come.

Methyl Chloride, Methyl Bromide and Methyl Iodide do all have an annual concentration varying with large amplitude over the season due to their short lifetimes. At Mt.Zeppelin monthly mean baseline mole fractions of CH_3Cl and CH_3Br show repetitive seasonal cycles from year-to-year. Mole fractions peak in the spring in common with many other trace gases (CH_4, N_2O, CO_2, CH_3CCl_3, CO and O_3), which are also measured at Mt.Zeppelin, due to their reaction with OH. CH_3Cl baseline mole fractions peak in spring slightly earlier than CH_3Br and reach a minimum in autumn as with CH_3Br. The soil sink has similar seasonality to the atmospheric sink (summer maximum), so observations may not be able to distinguish these sinks (OH + soils = 60% of CH_3Br sink and 85% of CH_3Cl sink).

The mean mixing ratio is 8.85 ppt for CH_3Br, and 515 ppt for CH_3Cl. The mean mixing ratio of CH_3I is 0.66 ppt for the period, and the trend is positive and growing. For Methyl Bromide and Methyl Chloride the trends are positive with growth rates of 0.40 and 20.9 ppt/year respectively, but the growth in the trends are negative at -0.82 and -17.0 ppt/year^2 respectively.

Chlorinated solvents are decreasing at Mt.Zeppelin in 2001 - 2003. The mixing ratio and growth rate in CCl_4 concentration in 2001 - 2003 are 30.5 ppt and -0.15 ppt/year. The growth in the trend is 1.15 ppt/year^2. For Carbone Tetrachloride the respective numbers are 93.9 ppt and 1.36 ppt/year. The trend is decreasing at a rate of 1.10 ppt/year^2. Dichloroethane, DCE, have a mixing ratio of 0.66 ppt and a slightly increasing growth rate of 0.12 ppt/year.

Once a major source of chlorine to the stratosphere, Methyl Chloroforms chlorine burden is now less than the major CFCs and HCFC-22. MC and HCFC-22 made up about 14 percent of the total chlorine burden in the atmosphere in 2003.

The Methyl Chloroform mixing ratio at Mt.Zeppelin has been declining exponentially since 2001 because of the rapid drop in emissions to low levels; global mixing ratios in 2000 were less than one-half of the peak observed in 1992. [Montzka et al. 2002] The rapid decline in emissions of Methyl Chloroform and its relatively short lifetime have together resulted in a rapidly decreasing mixing ratio during the period of investigation. The mean concentration of Methyl Chloroform is 34 ppt and the growth rate for 2001 - 2003 is -3.43 ppt/year and increasing at a rate of 1.00 ppt/year^2. The rate of decline observed for Methyl Chloroform (and chlorine from Methyl Chloroform) at Mt.Zeppelin during 2003 was about two-thirds of what it was in

2001. The mean mixing ratio at Mt.Zeppelin in 2003 was approximately 28.2 ppt, compared to 35.0 ppt observed in 2001. The atmospheric concentration of MC (CH_3CCl_3) will continue to decline, as it is no longer emitted to any significant extent. The slowing of the rate of decline is also expected as its reaction with OH removes residual CH_3CCl_3 from the global atmosphere.

The long term trends are, as already pointed out, hard to describe with only 3 years of data available, but together with the information we have about productions, losses and recycling of the compounds, we are able to estimate the trends. Figure 4.1 - 4.3 show the daily mean values and monthly mean background for all species in this document.
Declining European emissions have been observed for most anthropogenic chlorocarbons.

4.1 Seasonal cycles

The averaged seasonal cycles for HFC-152a, CH_3Cl, CH_3I, CH_3Br, CH_2Cl_2 and CH_2ClCH_2Cl at the Zeppelin station are clearly showing a late winter maximum and late summer minimum. Such behavior is associated with a compound whose predominant removal processing in the atmosphere is reaction with the OH radical. The OH concentration is varying from a summer maximum to a winter minimum. The late winter maximum is often moved toward spring, due to shifts in the wind pattern. The air mass trajectories show more frequent transport of air from industrialized areas in springtime than during the winter. The varying biological production in the ocean may also contribute to shift in the maximum toward springtime.

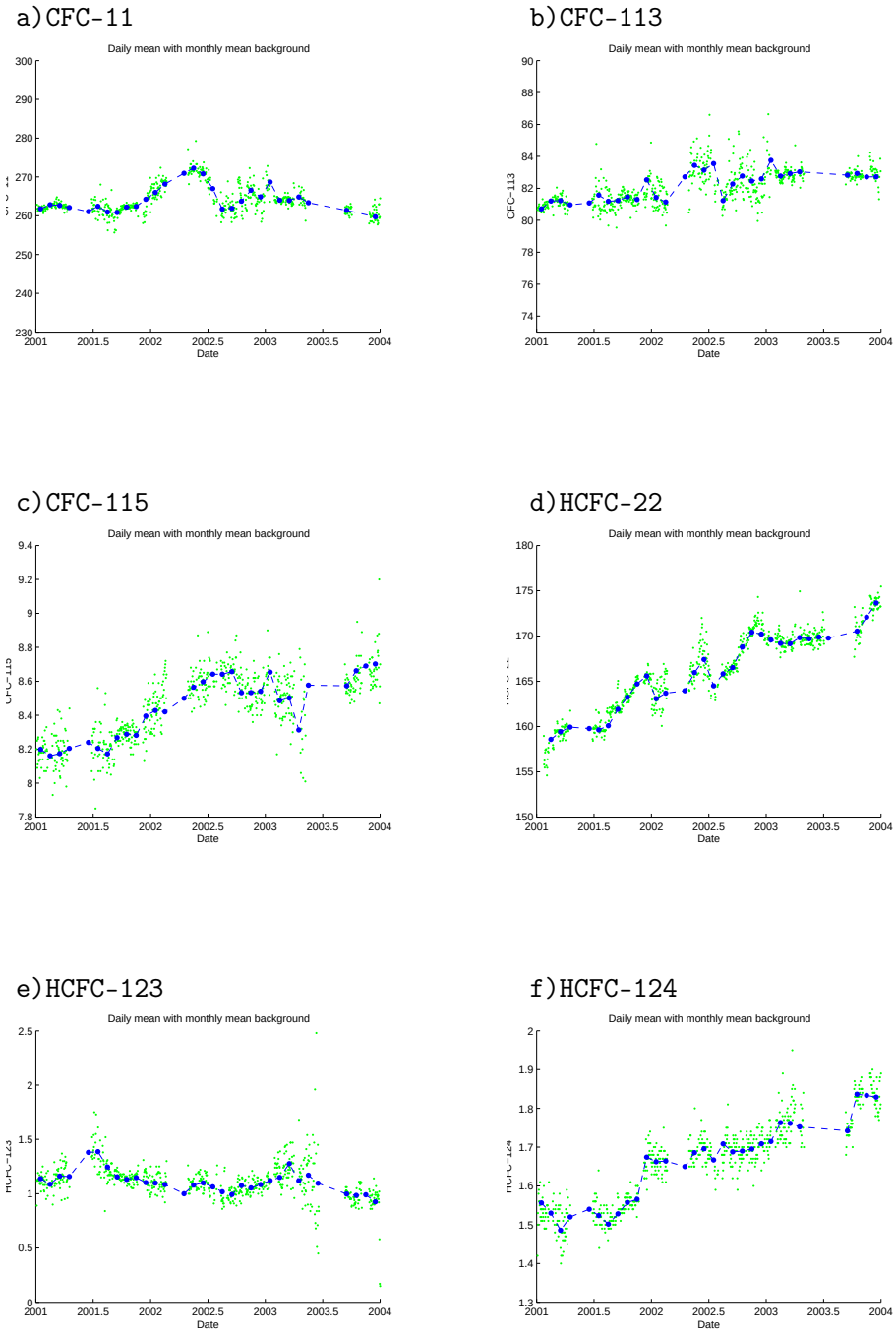


Figure 4.1: *CFCs and HCFCs. Monthly mean background values (blue) and daily mean concentrations (green) for 2001 - 2003.*

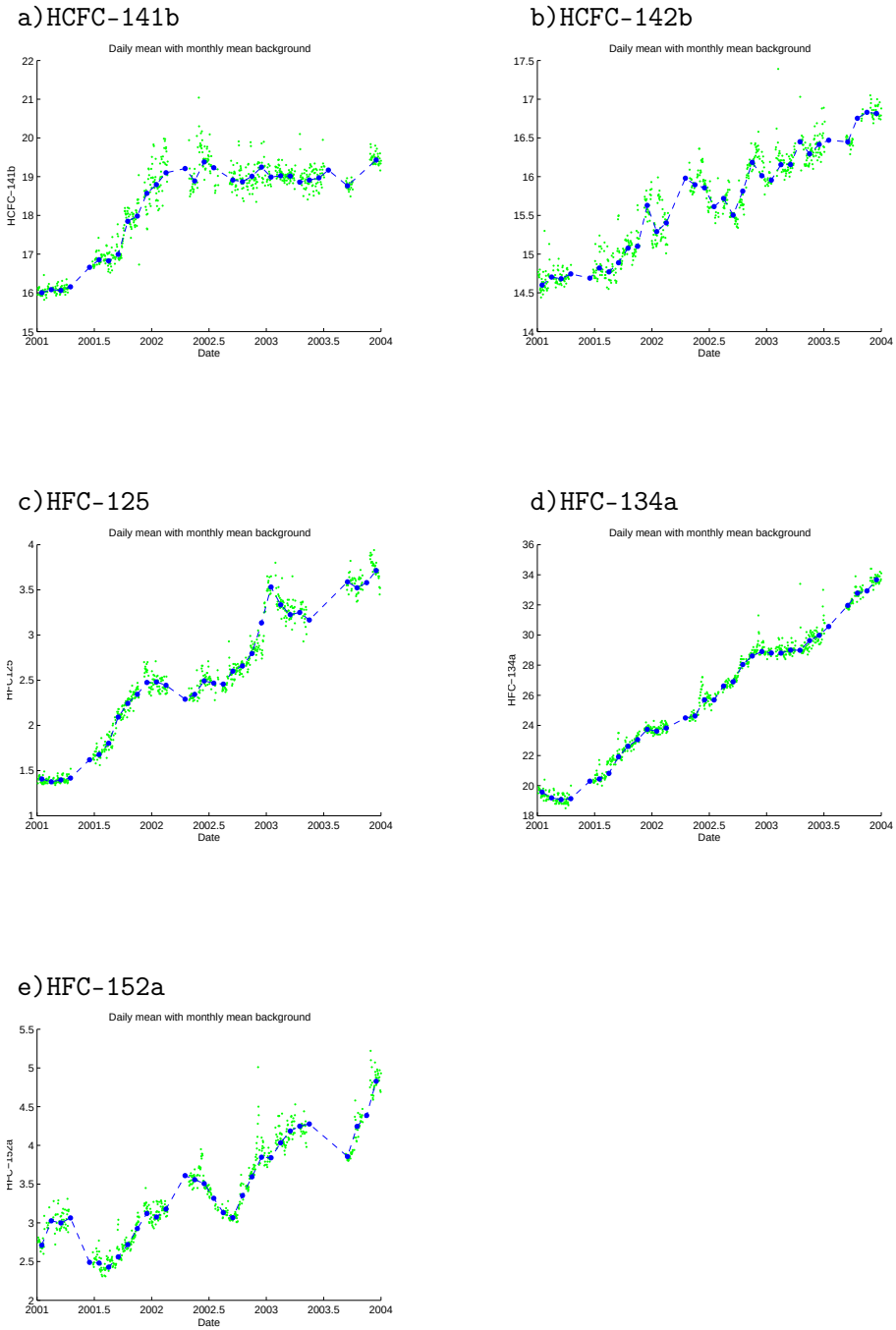


Figure 4.2: *HCFCs and HFCs. Monthly mean background values (blue) and daily mean concentrations (green) for 2001 - 2003.*

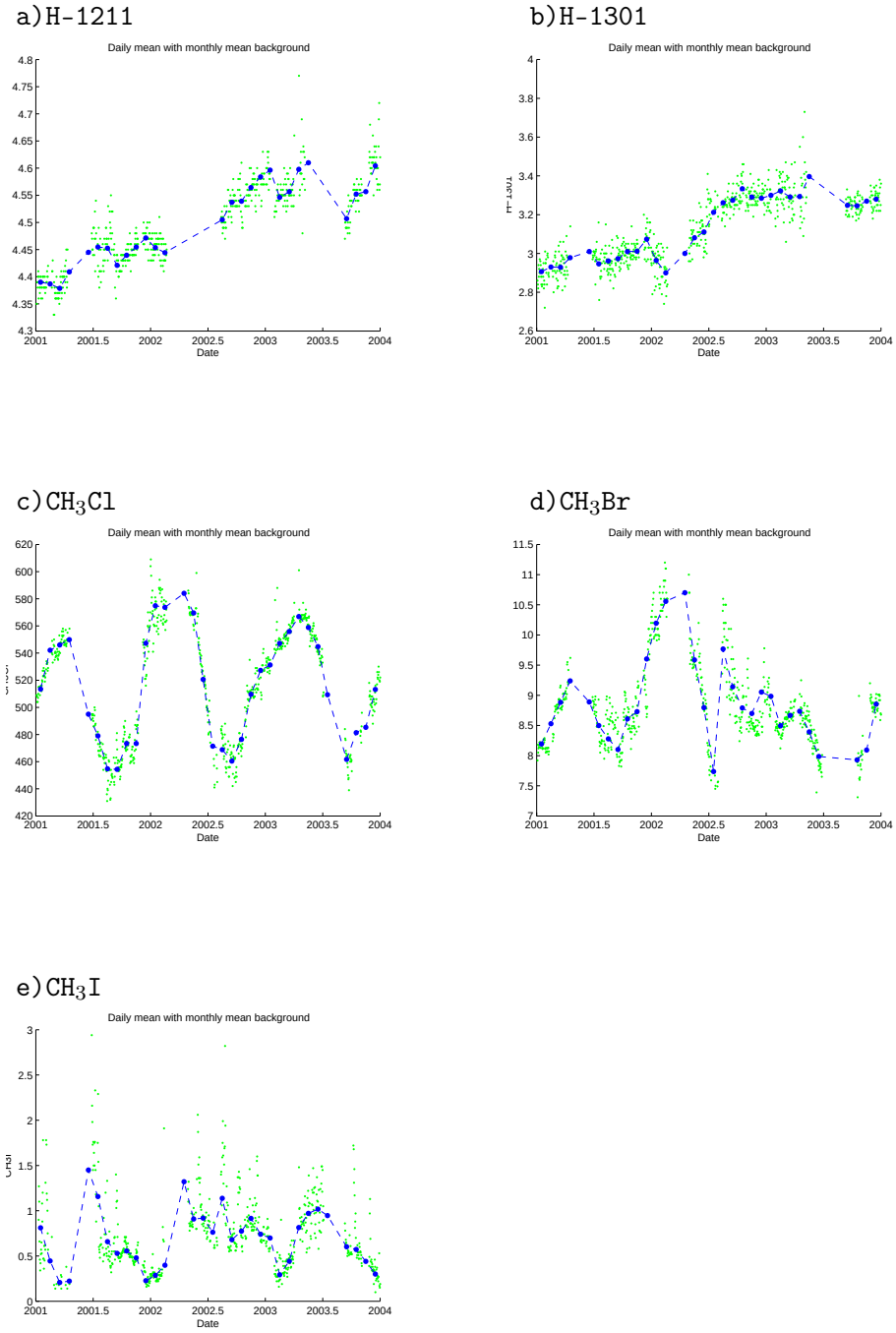


Figure 4.3: *Halons and chlorinated solvents. Monthly mean background values (blue) and daily mean concentrations (green) for 2001 - 2003.*

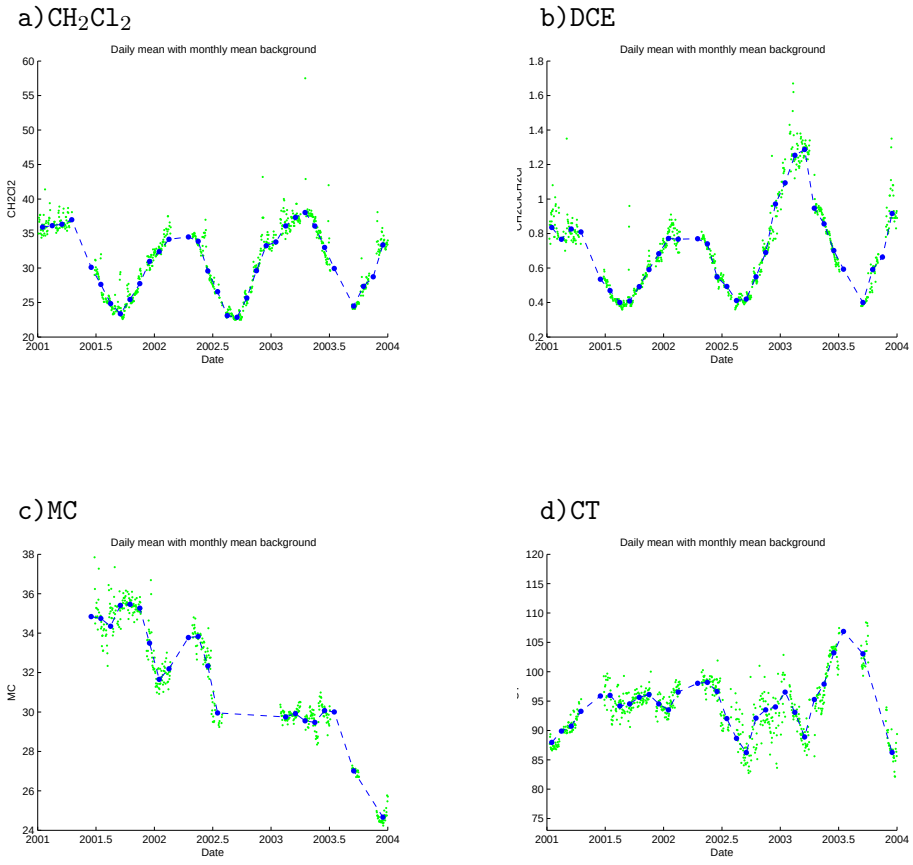


Figure 4.4: *Chlorinated solvents. Monthly mean background values (blue) and daily mean concentrations (green) for 2001 - 2003.*

Chapter 5

Synoptic scale episodes

5.1 Identification of episodes

The observed polluted events at Mt.Zeppelin are rare and small in amplitude, mainly due to long distance from urban source areas. Identification of polluted episodes in this thesis are used to evaluate European and Russian emissions, which can be found by using backward trajectories.
During 2001 - 2003 there are six main events that seem to be able to compare for more of the compounds.

Sept 13. - 17., 2001:
During mid-September 2001 the trajectories come from the European continent, mostly from Scandinavia and eastern Europe.

December 21., 2001:
Trajectories from the Russian continent, mostly from the eastern part.

May 28. - 30., 2002: The air mass trajectories show air coming from Scandinavia and Great Britain.

June 18., 2002
Trajectories from Novaja Semlja and the Russian continent.

December 3. - 7., 2002:
The air masses arriving at Mt.Zeppelin in this period do mainly come from eastern Europe (Poland) and Scandinavia, but also from Germany and France.

October 10., 2003:
Air mass backward trajectories show air from central Europe.

The trajectories are labeled in certain colors and plotted in figure 5.1 - 5.4 to visualize the different episodes. Except for one day of CFC-115 concentration higher than the background (June 2002); none of the CFCs seems to have concentration above the mean background for the mentioned events, indicating that the current emissions of the CFCs are small.

For HCFC-22, figure 5.1d), we can easily see two 2002 episodes, marked as air from the European continent, around 50% above the mean background. Also the European September 2001 event and Russian June 2002 events are seen, but at lower concentration levels.

For HCFC-123, figure 5.1e), we do not find any peaks in European or Russian sector events.

When it comes to HCFC-124, in figure 5.1f), there is one clearly seen event, from Russian sector in March 2003. This event in not included in the 6 events of major concern, and will not be included in further discussions.

For HCFC141b, figure 5.2a), we can clearly see the May 2002 episode. There are no measurements above the mean background for the December 2002 episode.

Considering HCFC-142b, figure 5.2b), we can again see the May 2002 and December 2002 events above the mean background.

HFC-125 does not seem to have peak values for any of the typically seen events.

For both HFC-134a and HFC-152a we find that almost all of the clearly seen events come from European sector, figure 5.2d) and e). The relatively new fluorocarbon and CFC-11 replacement HFC-134a (in use since 1990) is at a high rate represented from emissions from vehicles, concentrated in the US and Europe with 200 million vehicles each in the year 2000. The known event in May 2002 is easily seen for both HFC-134a and HFC-152a, with peak concentrations about 50% higher than the estimated background. We do also see an event in December 2002, with trajectories from European sector.

Both H-1211 and H-1301, figure 5.3a) and b), have some gaps in the data. There is no specific pattern in the elevated peak concentration from different sectors.

When it comes to CH_3Cl, figure 5.3c), and CH_3Br, figure 5.3d), none of the events of interest have data measurements above the mean background concentration.

CH_3I, figure 5.3e), is showing elevated concentration levels when the air mass trajectories come from Europe in May 2002 and in December 2002.

In figure 5.4a), the CH_2Cl_2 daily means show peak values up to 10 times the mean background concentration for all the European episodes of interest.

DCE, figure 5.4b), is showing peak values for two of the European events, the May 2002 and December 2002 events. The December 2003 event is of less

interest, due to short duration of the event, and air mostly from undefined sector.

MC and CT, figure 5.4c) and d), do not have any seen elevated peaks above the mean background.

5.1.1 The use of data

Observations

By using a combination of air mass trajectories and the sector information, we observe that days with elevated concentration levels in most cases are associated with air from a non-Arctic sector.

For all components the individual daily values are naturally located below and above the monthly mean. Episodes can only be identified when the amplitude is large compared to the noise from the instrument.

The pollution events do also contain essential information about regional (European and Russian) emissions.

Meteorology

The meteorology at the Svalbard islands must be mentioned. The transport pattern varies according to season and to the meteorological situation, and the events with Arctic Haze and other pollutants alternate with periods in which the air masses are extremely clean. In fall, winter and spring, the circulation often favor transport into the Arctic from mid-latitudinal regions with prominent pollution sources. In summer the circulation in the Arctic atmosphere is essentially local and confined within the region. Few and small emissions are resulting in very low values of concentration compared to other measuring sites.

5.1.2 Results

The relationship between the atmospheric concentration of two long-lived trace species could be used to quantify their relative source strengths. However, this is not done in this thesis. Here we rather investigate the common source sectors, both in industry and in geographic location. In this document we are evaluating correlation between the gases in 3 different experiments. First we are correlating the gases for the 3 year period of interest as a whole, named experiment (A). In the second experiment, (B), the correlations are based on days with air mass trajectories coming from European or Russian sector. Finally, in experiment (C), we separate the two sectors to localize specific source regions.

Table 5.1 and 5.2 show the correlation factors between the different gases in SOGE for the 2001 - 2003 period as a whole, experiment (A). When taking a closer look at the results showed in the tables, we find a cluster of some good correlating species. HFC-134a, HFC-152a, HCFC-22, HCFC-142b and CH_2Cl_2 do all have internal correlation factors above 0.4.

The best correlations are between

HFC-152a and CH2Cl2; 0.74

HFC-134a and HFC-152a; 0.70,

HFC-134a and CH_2Cl_2; 0.64

HFC-134a and HCFC-22; 0.60,

and between HFC-152a and HCFC-22; 0.50.

The correlation factors for these compounds correlated with HCFC-142b are slightly below 0.50.

To explain the good internal correlations within the above mentioned group, we must take factors like sources and sinks, and production and fields of use for the different compounds into account.

Methylene Dichloride (CH_2Cl_2) does not have any significant natural sources. The major sources of CH_2Cl_2 are from foam plastic production, metal cleaning and other solvent uses. The good correlations with HFC-134a and HFC-152a are assumed to be due the compounds common source areas and common fields of use. All three gases are CFC-11 replacements. In general one can say that CH_2Cl_2 shows good correlations with the gases in the group defined above for the 2001 - 2003 period as a whole. The good correlation between HCFC-22 and HCFC142b might be a result of the two gases common fields of use. Both the gases have been developed as replacements for CFC-12 in stationary air-conditioning and refrigeration equipment. The correlation between HFC-125 and HFC-134a is relatively good in experiment (A). A typically blend of HFC-125 and HFC-134a has been formulated as a replacement for HCFC-22 in new or existing air-conditioning equipment and heat pumps.

The correlation between CFC-11 and CFC-113 should also be mentioned. It is as high as 0.64, mainly due to their common fields of use, and due to the fact that the two compounds have the same internal restrictions within the different sectors.

CH_3Br and CH_3Cl have a correlation of 0.55. Although their sources are largely natural, human induced changes to their emissions may result from land-use and climate changes. We do not find any typically good correlations between CH_3 Br and CH_3Cl and other compounds for the general case. HCFC-141b is a CFC-11 replacement and the two gases are therefore showing a good correlation. This is discussed in detail later. For the other components there are only low correlations, not worth mentioning in the general case.

Episodes

For most of the species, the concentrations rapidly increase as the wind flow patterns shift to south west or east, and reach maximum values in air parcels traveling from the European continent or Russian industrialized areas. As the wind shifts back to the north and west the concentrations begin to drop and they return to their background levels. Coastal-seawater sources are possible sources for CH_3Cl. [Rhew et al., 2000] Other species that contains Cl may also have elevated concentration levels when the wind comes from an oceanic sector. As already mentioned, most of the events occur during the northern hemisphere fall, winter and spring. Out of 1095 possible days for pollution events, we find polluted episodes in 19 - 23 days in European sector, and 13 - 19 days in Russian sector. The numbers are based on averages for all the components. In experiment (B) isolated days with air mass trajectories either from European or from Russian sector are separated. The correlation factors are shown in table 5.3 and 5.4. The further separated European and Russian sectors in experiment (C) give us correlation factors as shown in table 5.5 and 5.6 (European) and table 5.7 and 5.8 (Russian).

In experiment (A) we found that HFC-134a, HFC-152a, HCFC-22, HCFC-142b and CH_2Cl_2 made a cluster of species with good internal correlation. While investigating the cases when the air comes from European sector or Russian sector only, i.e. assumed separated polluted events and not including other sectors, we find even better correlations within this cluster. The best correlation factors are between HFC-152a and CH_2Cl_2; 0.90, and between HFC-134a and HFC-152a; 0.84. All results are shown in table 5.3 and 5.4. The fact that the correlations are better in the experiment with separated events (B) than in the all-trajectory experiment (A) indicates that the air defined as background is much cleaner than air coming from Europe and/or Russia.

There are some other compounds not included in the group mentioned above, that show better correlations for case (B) than case (A) as well, indicating polluted air from one or both of the two 'polluted' sectors. Carbon Tetrachloride (CT) is a compound that has to be mentioned here. From having a correlation factor above 0.5 with Methyl Chloroform only in case (A), the number of cases with correlation factors better than 0.5 between MC and other components rises to 8 in case (B). The best correlation, 0.70, is between CT and H-1211. Methyl Chloroform show good correlation with CFC-11 and CFC-113 in the separated case (B), with correlation coefficients between 0.5 and 0.6. We do not see this correlation in the general case (A). These strong correlations for MC will be discussed in detail later.

CH_3Cl shows better correlations with the gases in the 'group' in case (B) than in case (A). This correlation will be discussed later. In case of trajectories coming from all sectors, H-1211 and H-1301 show no correlation with other compounds. When filtering out European and Russian air only, we find good correlations for H-1211 with HFC-125, HFC-134a, HFC-152a, CFC-11 HCFC-141b and CH_2Cl_2. Those good correlations are most probably due

to the frequent use of H-1211 as a fire suppressant in industrialized areas, where the other gases above have their main sources as well.

The correlation between CFC-11 and CFC-113 do not show any clear change from experiment (A). CFC-113 shows better correlations with CFC-115, CH_3Br and MC in experiment (B) than in experiment (A).

Taking a closer look at the European and Russian sectors separately, we are able to find out more about regional emissions, and to explain some of the good correlations found in experiment (B) more in detail. In general it seems that European sector correlations are better than Russian sector correlations for most of the gases. This might be due to the fact that there are more industrialized regions in Europe than in Russia. The winds pattern favor the European sector and this leads to more frequent elevated European events, and thereby better data representation.

All the compounds in the earlier defined cluster show internal correlation factors above 0.57 for European sector (table 5.5 and 5.6). The best correlations are between CH_2Cl_2 and HFC-134a and HFC-152a. These good correlations can easily be explained by taking in account that all the three components are frequently used in the industrialized parts of Europe. For Russian sector (table 5.7 and 5.8) the correlations between CH_2Cl_2 and HFC-134a and HFC-152a are less good. This might be explained by less frequent use of the HFCs in this sector. As we further will see, there are better correlations in European sector than in Russian sector for other species as well.

CFC-11 and CFC-113 do not correlate in Russian sector, but they show good correlation in all other cases. This is an indication of differences in production, fields of use and/or deposition for the two gases in Russia. CFC-11 and CFC-113 seems to have a similar internal behavior in European sector. This indicates that the phase-out of the two species are in agreement with the Montreal Protocol.

In Russian sector, as the only place, we find good correlation between CFC-11 and CFC-115. The two gases do not have any common fields of use, so the good correlation might be due to their relative emission strengths only. There is a strong correlation between CFC-11 and HCFC-141b in the Russian sector, which we do not see in the other experiments. HCFC-141b is a CFC-11 replacement, and the correlation of 0.46 can easily be explained by taking in to account that both the gases are in use in Russian sector, while CFC-11 is phased out in European sector (correlation factor of 0.12). This is shown by scatterplots in figure 5.5 a) and b). We can easily see the outliers in the plots, denoting the real events. The second generation-replacement HFC-152a is currently replacing HCFC-141b. The correlation between the two gases are 0.37 in Russian sector, and 0.15 in the European sector. The low correlation for European sector can be explained by evaluating the European emission source strengths. The emissions of HCFC-141b are declining while the HFC-152a emissions are stable in Europe in 2000 -

2003 (figure 5.6e) [Manning et al., 2003].

HFC-134a is, like HFC-152a, a replacement for HCFC-141b. Both HFC-134a and HCFC-141b are present in use in European sector and should therefore correlate. From table 5.5 we find the correlation factor to be 0.47. For Russian sector we do not find any correlation (0.05), which indicates that the gases have different fields and degrees of use within this sector. One can assume that HCFC-141b is more common than HFC-134a in Russia.

The good correlations found in experiment (B) for HFC-134a and HFC-152a with compounds like HCFC-22, HCFC-142b and CH_2Cl_2 come from high concentrations observed in European sector. For Russian sector all those internal correlations, except for the one between HFC-134a and HCFC-22, are lower than 0.34. Those results can be explained by assuming that the strength of the events including components like HFC-134a and HFC-152a are at the same level in Europe and the developed countries, but at different (lower) levels in the developing countries. We find that both HFC-134a and HFC-152a have higher peak values in events from European sector than in events from Russian sector. This is most probably due to the more frequent production and use of the two species within Europe than in Russia. HCFC-22, and its second generation substitute HFC-134a, substitute CFCs to a higher degree in Europe, which can be seen in the correlation matrixes. CH_2Cl_2 is frequently used as an industrial solvent in Europe, which results in good correlations with a lot of other species.

The correlation between HCFC-141b and CFC-115 is much better for the Russian sector than for the European sector. Both gases are present in use in Russia, while CFC-115 are about to level out in Europe.

CH_3Cl shows good correlations with all the HFCs and the chlorinated solvents in the 'group' in European sector. It is not possible to detect any strong events from Russian sector for the two latter compounds, which could contribute to this seen correlation. CH_3Cl is used as a soil and crop fumigant mostly in European farming countries, but there are few common fields of use with the HFCs, and it is therefore not included in the 'group'. For Russian sector we do only find good correlation with HFC-152a, still not very high. The best CH_3Cl correlation for Russian sector is found when comparing the gas to CH_3Br.

CH_2Cl_2 shows, as mentioned above, better correlations with the gases in the 'group' for European sector than for Russian sector. Air mass trajectories from Russia have, due to less frequent use of the component in this sector, on average lower concentrations of CH_2Cl_2 than European trajectories. Methylene Dichloride is no longer expected to be a significant substitute for CFC-11. The correlation between CH_2Cl_2 and CFC-115 is negative for European sector, and positive and above 0.5 for Russian sector. This is according to what we expect when concerning the banning of CFC-115 in the developed countries. In Russia and Asia CFC-115 is about to be phased out

in 2020. CH_2Cl_2 and CH_2ClCH_2Cl do also have different behavior between the two sectors. The correlation for European sector is good, 0.70. When the air mass trajectories come from Russia, the correlation between those two gases are close to zero. To evaluate this result, we must know more about emissions, deposition, waste and so on for the two components.

DCE seems to show better correlations with the species in the 'group' for European sector, than for Russian sector. The only good correlation for this compound for Russian sector is found when comparing to CFC-113.

Both CFC-11 and MC are still in use on the Russian continent, but none of them seem to have peak values above the clean background during the 13-19 possible 'polluted' days of interest (figure 5.1a and 5.2c). The correlation between MC and DCE for European sector is negative. DCE has a lot more observed events than MC for air masses coming from the continental Europe than from other places. For Russian sector Methyl Chloroform shows good correlation with both CFC-11 and CFC-113. These observations, together with the conclusions made above, are indications of the fact that Methyl Chloroform is banned in the developed countries but still not phased out in Asia and Russia. During episodes with prevailing winds from the European continent, Scandinavia and/or the Great Britain, none of the air mass trajectories show elevated levels for MC concentration. For Russian sector Methyl Chloroform shows good correlations with both CFC-11 and CFC-113.

The good correlations for Carbone Tetrachloride seen in experiment (B) are in experiment (C) found to be a combination of good correlation with species in both Russian and European sector. CT have more fields of use, which may lead to different correlation factors between the two sectors. The component is used both as a household cleaner and as a CFC-11 feedstock. Figure 5.5 - 5.7 show some examples of correlation plots of selected events for two gases for European and Russian sector. These figures give us important information about the correlation between the two compounds in sector E (Europe) and in sector R (Russia), about sources, fields of use, banning and so on., and of validation of the best fit background baseline.

By combining information from the plots with the correlation matrixes it is possible to cluster the species into groups.

In sector E (Europe), as already mentioned above, typically

- **HFC-134a, HFC-152a, HCFC-22, HCFC-142b, CH_3Cl, CH_2Cl_2**

will make such a group.

In sector R (Russia) we can expect the groups to be organized slightly different, because the Montreal Protocol affected the developed countries only. Good correlation between HFC-134a and CFC-113 is an example of two gases that show different cluster patten form one sector to another.

- **CFC-11, CFC-113, CFC-115, HCFC-141b, MC, DCE**

might make a group of species in the Russian sector.

When working with the European and Russian events at Mt.Zeppelin in 2001 - 2003, we found that a great part of the correlation factors showed differences from one sector to the other. Only the most obvious and significant correlations are discussed in this thesis.
Taking a closer look at figure 5.5 - 5.7, which show scatterplots of some of the gases after extracting the background, we see that some points in the plots are located very close to origo. Those scatterpoints are worth taking a closer look at. They can be real events, but they might in addition also be influenced by noise from the instrument. Observations that should be taken in account while finding the baseline might be among those points as well. We have briefly tried to filter out some of the points, to test the possibility of obtaining better correlation factors. Two different filters are applied to the time series. The results are shown in figure 5.7.

We first filter out the values closer to zero than one standard deviation. The results for HFC-134a and HFC-152a are shown in figure 5.7a). The number of valid data points after the filtering is small, for Russian sector only 3, and for European sector 7. Calculating correlation factors upon such small number of samples are leading to uncertain results. To improve the data cover included in the correlation calculations, we have done a second experiment with a lower filter value. figure 5.7b) is showing data points which have passed through a $1/2$ standard deviation filter. The number of valid data points is then increasing to 5 for the Russian sector and 11 for the European sector. The same experiments are shown for HFC-134a and HCFC-22, figure 5.7 c) and d). As for the other correlations, the number of samples is too small to give the valid information.
While doing this experiment for the other gases included in this paper, we find that the removing of data points very often is above 80%, even when using $1/2$ standard deviation as a filter value. This lead to the conclusion that this filtering method not should be used on time series as short as 3 years, when studying events at Mt. Zeppelin. There are too few events taking place within these 3 years, and the air at this remote arctic station is basically clean.

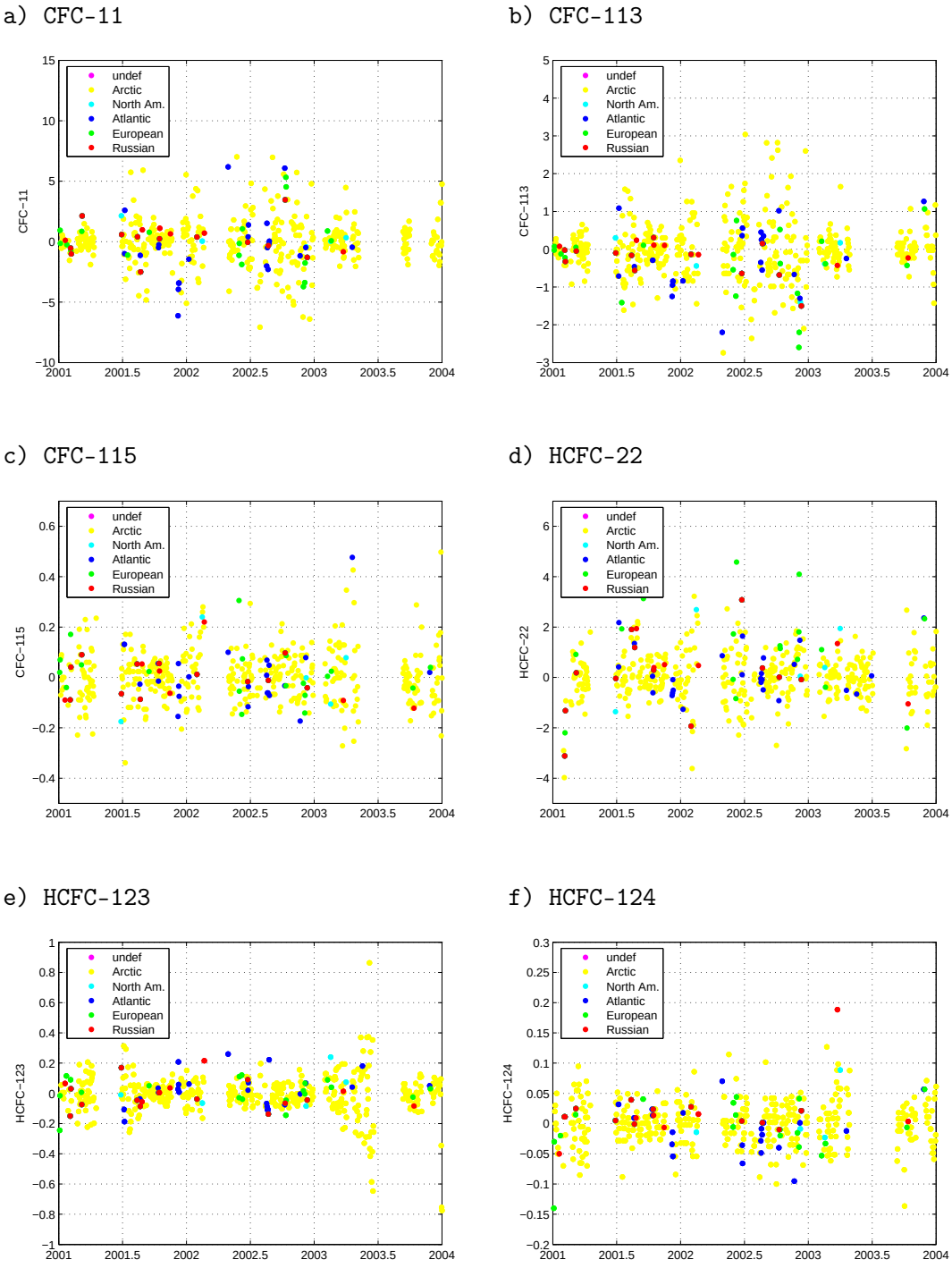
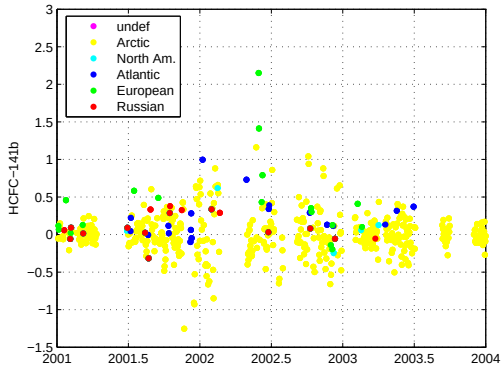
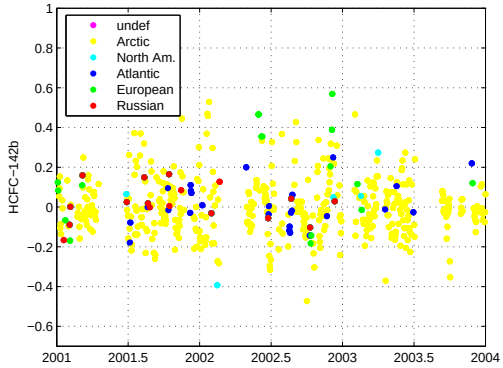


Figure 5.1: *Deviation from the monthly mean background*

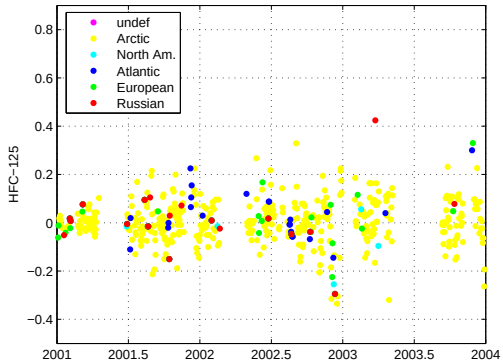
a) HCFC-141b



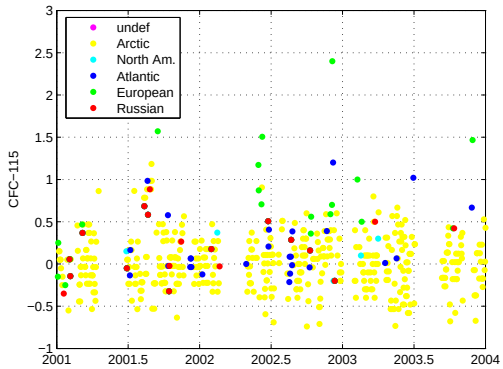
b) HCFC-142b



c) HFC-125



d) HFC-134a



e) HFC-152a

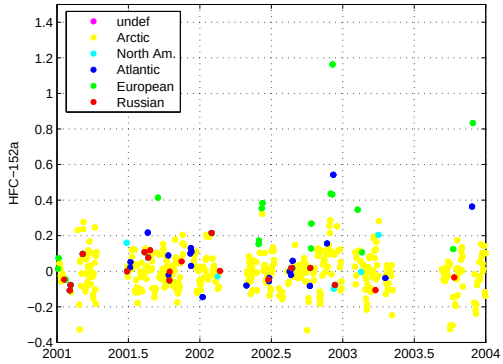


Figure 5.2: *Deviation from the monthly mean background, daily values. Sectors in different colors.*

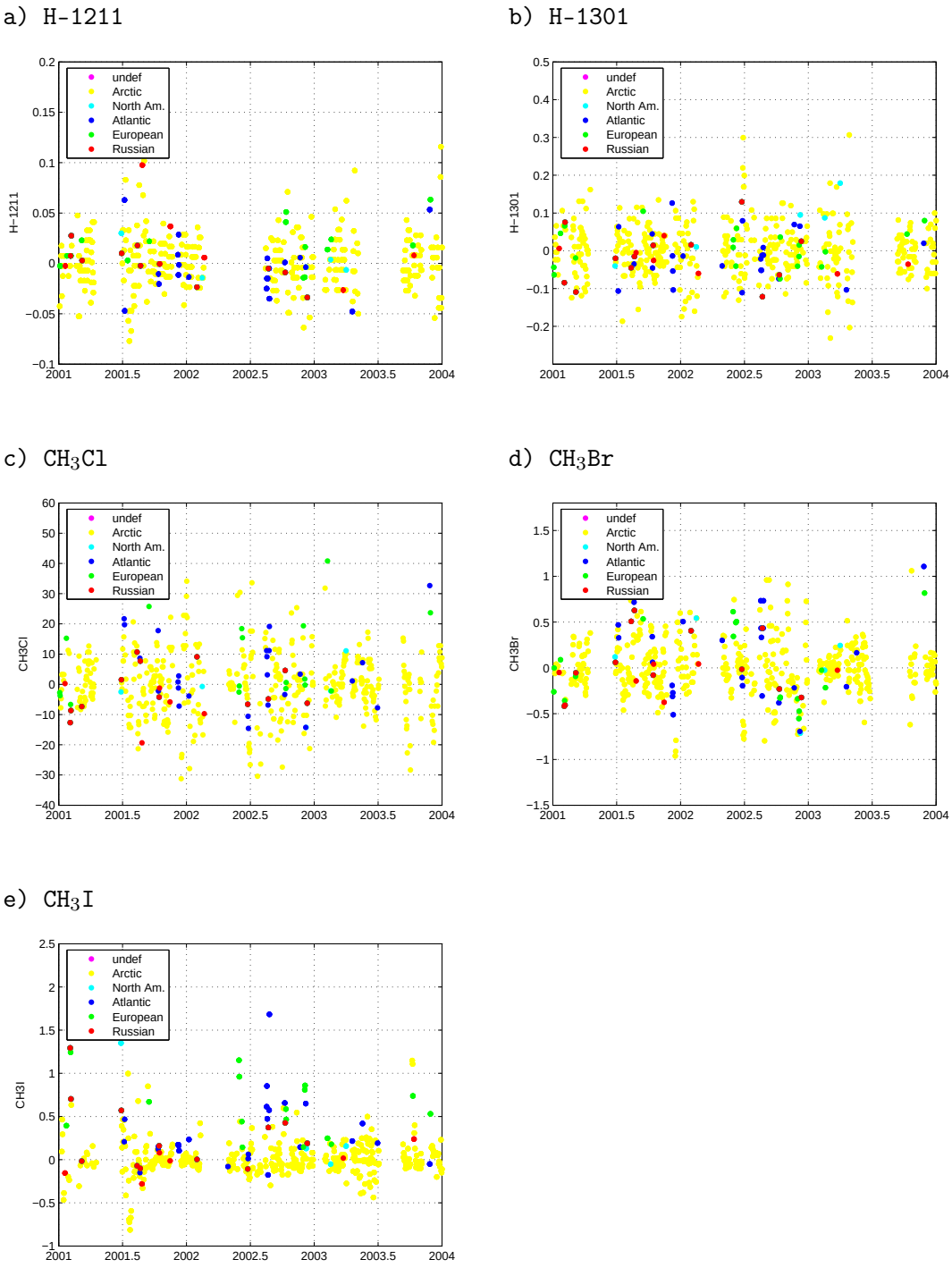


Figure 5.3: *Deviation from the monthly mean background, daily values. Sectors in different colors.*

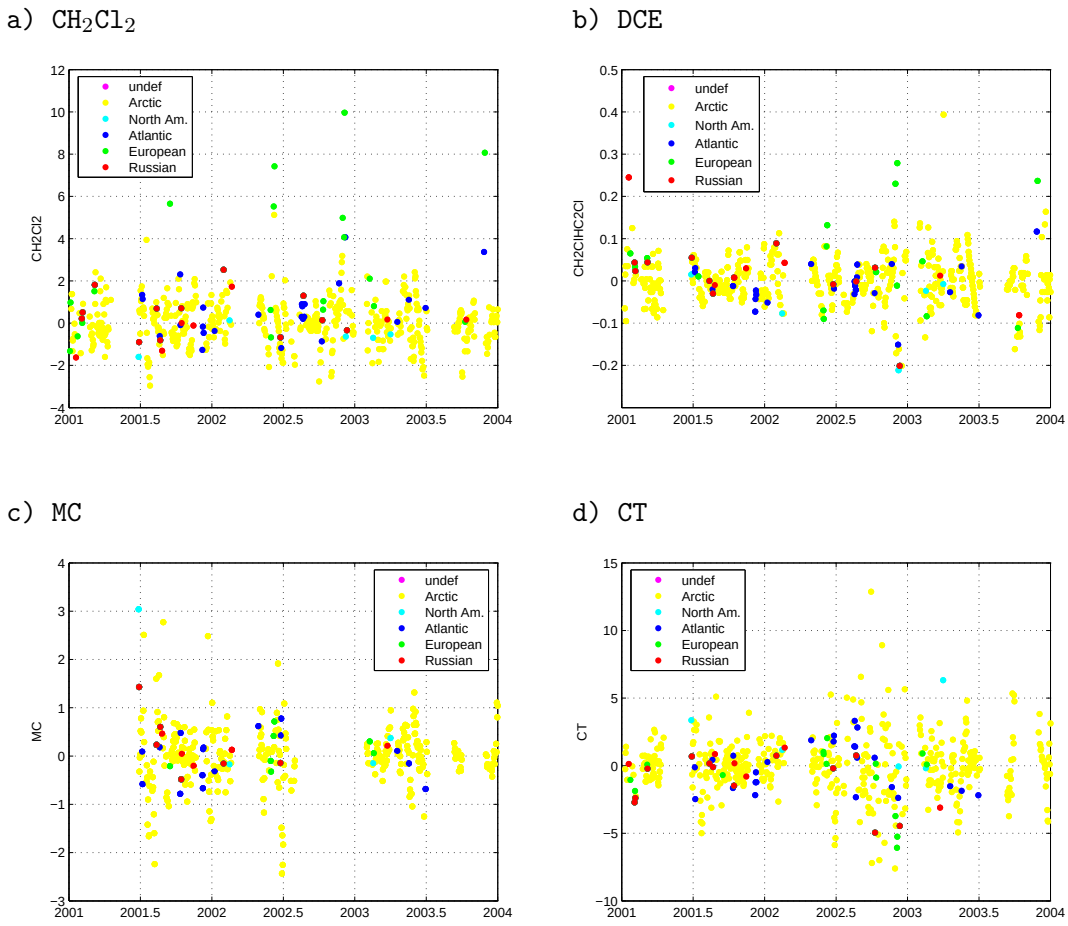


Figure 5.4: *Deviation from the monthly mean background, daily values. Sectors in different colors.*

Compound .	**HFC 125**	**HFC 134a**	**HFC 152a**	**CFC 11**	**CFC 113**	**CFC 115**	**HCFC 22**	**HCFC 123**	**HCFC 124**	**HCFC 141b**	**HCFC 142b**	**H 1211**	**H 1301**
HFC-125	1												
HFC-134a	**0.49**	1											
HFC-152a	0.14	**0.70**	1										
CFC-11	0.12	0.06	-0.12	1									
CFC-113	0.17	-0.02	-0.05	**0.65**	1								
CFC-115	-0.06	0.09	0.05	0.15	0.08	1							
HCFC-22	0.11	**0.60**	**0.50**	0.12	0.01	0.09	1						
HCFC-123	0.10	0.12	0.15	0.01	-0.02	0.03	0.07	1					
HCFC-124	0.14	0.30	0.22	0.21	0.09	0.10	0.22	0.01	1				
HCFC-141b	0.14	0.35	0.19	**0.46**	0.34	0.19	0.28	0.09	0.16	1			
HCFC-142b	0.05	**0.41**	**0.49**	0.15	0.05	-0.02	0.37	0.08	0.23	0.23	1		
H-1211	0.19	0.35	0.27	0.35	0.37	0.05	0.19	0.17	0.13	0.24	0.15	1	
H-1301	0.06	0.23	0.10	-0.02	0.03	0.14	0.16	0.08	0.10	0.05	-0.01	0.04	1
CH_3Cl	0.04	0.14	0.27	0.16	0.12	0.04	0.12	0.04	0.11	0.24	0.18	0.14	-0.02
CH_3Br	0.05	0.07	0.06	0.16	0.17	0.11	0.17	0.01	0.14	0.38	0.02	0.16	-0.03
CH_3I	0.01	0.29	0.29	0.06	0.02	-0.04	0.07	0.11	0.10	0.35	0.19	0.10	0
CH_2Cl_2	0.12	**0.64**	**0.74**	0.01	-0.03	0.05	**0.47**	0.19	0.28	0.35	**0.42**	0.33	0.08
DCE	0.23	0.20	0.39	0.20	0.16	0.03	0.20	0.10	0.14	0.14	0.24	0.21	0.04
MC	0.08	0.06	0.19	0.27	0.23	-0.04	0.11	0.03	0.07	0.11	0.09	0.23	-0.14
CT	0.27	0.09	0.19	0.35	0.16	-0.04	0.12	-0.04	0.02	0.20	-0.01	0.20	0

Table 5.1: *Correlation coefficients for the components used in this document. Correlations better than 0.4 are showed in bold text. Numbers are based on all 2001-2003 data. Table part 1*

Compound	CH_3Cl	CH_3Br	CH_3I	CH_2Cl_2	DCE	MC	CT
HFC-134a							
HFC-152a							
CFC-11							
CFC-113							
CFC-115							
HCFC-22							
HCFC-123							
HCFC-124							
HCFC-141b							
HCFC-142b							
H-1211							
H-1301							
CH_3Cl	1						
CH_3Br	**0.55**	1					
CH_3I	0.18	0.18	1				
CH_2Cl_2	**0.41**	0.27	0.37	1			
DCE	0.28	0.16	0.04	**0.50**	1		
MC	0.18	0.24	0.18	0.14	0.15	1	
CT	0.11	0.30	0.07	0.17	0.13	**0.45**	1

Table 5.2: *Correlation coefficients for the components in this document. Correlations better than 0.4 are showed in bold text. Numbers based on all 2001-2003 data. Table part 2*

Compound .	**HFC 125**	**HFC 134a**	**HFC 152a**	**CFC 11**	**CFC 113**	**CFC 115**	**HCFC 22**	**HCFC 123**	**HCFC 124**	**HCFC 141b**	**HCFC 142b**	**H 1211**	**H 1301**
HFC-125	1												
HFC-134a	0.39	1											
HFC-152a	0.25	**0.84**	1										
CFC-11	0.07	-0.05	-0.17	1									
CFC-113	0.34	-0.09	-0.16	**0.63**	1								
CFC-115	-0.11	-0.03	-0.08	0.37	**0.43**	1							
HCFC-22	0.28	**0.70**	**0.56**	0.14	-0.01	-0.02	1						
HCFC-123	0.02	0.11	0.20	-0.08	-0.01	0.07	0.12	1					
HCFC-124	**0.47**	0.37	0.18	-0.03	0.13	0.04	0.31	0.25	1				
HCFC-141b	0.11	**0.49**	0.23	0.17	0.17	0.38	0.27	0.12	0.17	1			
HCFC-142b	0.10	**0.66**	**0.57**	-0.36	-0.32	-0.80	**0.53**	0.11	0.27	**0.53**	1		
H-1211	**0.43**	**0.51**	**0.50**	**0.47**	0.27	-0.01	0.31	0.17	0.20	**0.47**	0.06	1	
H-1301	-0.06	0.15	0.14	0.03	0.17	0.24	0.13	0.04	0.10	0.10	0.07	0.02	1
CH_3Cl	0.36	**0.47**	**0.49**	0.03	0.16	-0.08	0.31	0.09	0.12	0.20	0.34	0.30	0.17
CH_3Br	0.32	0.38	0.20	0.14	**0.48**	0.26	0.28	0.02	0.32	**0.55**	0.23	0.39	0.18
CH_3I	-0.17	0.22	0.27	-0.08	-0.07	0.03	-0.29	-0.03	-0.04	0.36	0.25	0.17	0.10
CH_2Cl_2	0.33	**0.77**	**0.90**	-0.19	-0.08	-0.07	**0.52**	0.18	0.33	0.21	**0.59**	**0.49**	0.09
DCE	0.30	**0.40**	**0.56**	0.05	0.15	0.08	0.38	0.31	0.20	0.05	**0.40**	0.25	0.19
MC	0.12	-0.04	0.02	**0.52**	**0.60**	0.21	-0.14	0.37	0.02	-0.18	-0.41	0.15	-0.08
CT	**0.52**	0.36	**0.48**	**0.43**	0.35	-0.02	0.19	-0.01	0.21	0.35	0.03	**0.70**	0.13

Table 5.3: *Correlation factors for some gases based of known episodes in either European or Russian sector. Correlations better than 0.4 are showed in bold text. Numbers based on 2001-2003 data. Part 1*

Compound	CH_3Cl	CH_3Br	CH_3I	CH_2Cl_2	DCE	MC	CT
HFC-125							
HFC-134a							
HFC-152a							
CFC-11							
CFC-113							
CFC-115							
HCFC-22							
HCFC-123							
HCFC-124							
HCFC-141b							
HCFC-142b							
H-1211							
H-1301							
CH_3Cl	1						
CH_3Br	**0.54**	1					
CH_3I	0.04	-0.02	1				
CH_2Cl_2	**0.53**	0.29	0.20	1			
DCE	**0.41**	0.14	-0.04	**0.62**	1		
MC	0.09	0.23	0.05	-0,04	-0.08	1	
CT	**0.41**	**0.53**	0.12	**0.50**	0.24	**0.58**	1

Table 5.4: *Correlation factors for some gases based of known episodes in either European or Russian sector. Correlations better than 0.4 are showed in bold text. Numbers based on 2001-2003 data. Part 2*

Compound .	**HFC 125**	**HFC 134a**	**HFC 152a**	**CFC 11**	**CFC 113**	CFC **115**	**HCFC 22**	**HCFC 123**	**HCFC 124**	**HCFC 141b**	**HCFC 142b**	**H 1211**	**H 1301**
HFC-125	1												
HFC-134a	**0.41**	1											
HFC-152a	0.32	**0.86**	1										
CFC-11	0.27	-0.09	-0.23	1									
CFC-113	**0.61**	-0.13	-0.23	**0.62**	1								
CFC-115	0.28	0.03	-0.11	0.27	0.35	1							
HCFC-22	0.20	**0.73**	**0.58**	0.15	-0.04	-0.04	1						
HCFC-123	0.10	0.21	0.26	-0.21	0.02	-0.12	0.04	1					
HCFC-124	0.26	0.37	0.29	-0.05	0.18	0.03	0.25	0.34	1				
HCFC-141b	0.26	**0.47**	0.15	0.12	0.19	**0.46**	0.27	0.11	0.24	1			
HCFC-142b	0.03	**0.70**	**0.58**	-0.41	-0.32	-0.06	**0.54**	0.24	0.24	**0.55**	1		
H-1211	**0.56**	**0.41**	0.34	**0.55**	0.38	0.19	0.32	0.30	0.38	**0.46**	-0.03	1	
H-1301	0.13	0.24	0.20	-0.07	0.05	0.12	0.20	**0.5**	0.31	0.19	0.15	0.22	1
CH_3Cl	**0.49**	**0.44**	**0.47**	-0.01	0.13	-0.14	0.36	0.33	0.05	0.15	0.29	0.27	1
CH_3Br	**0.53**	0.34	0.11	0.03	**0.41**	0.15	0.28	0.11	**0.40**	**0.59**	0.32	0.30	0.15
CH_3I	0.10	0.13	0.17	-0.12	-0.09	0.11	-0.32	0.09	-0.01	0.32	0.19	0.03	0.08
CH_2Cl_2	0.36	**0.79**	**0.90**	-0.28	-0.16	-0.12	**0.53**	0.20	**0.42**	0.12	**0.59**	0.28	0.16
DCE	**0.41**	**0.55**	**0.60**	0	0.12	-0.03	0.37	0.20	0.37	0.02	**0.43**	0.23	0.22
MC	0.38	-0.04	0.04	0.37	0.39	-0.32	-0.32	0.20	-0.14	-0.31	-0.21	0.26	-0.38
CT	**0.62**	0.28	**0.41**	0.37	**0.41**	0.09	0.16	0.07	0.37	**0.48**	0	**0.52**	0.25

Table 5.5: *Correlation factors for some gases based of known episodes in European sector. Correlations better than 0.4 are showed in bold text. Numbers based on 2001-2003 data. Part 1*

Compound	CH_3Cl	CH_3Br	CH_3I	CH_2Cl_2	DCE	MC	CT
HFC-125							
HFC-134a							
HFC-152a							
CFC-11							
CFC-113							
CFC-115							
HCFC-22							
HCFC-123							
HCFC-124							
HCFC-141b							
HCFC-142b							
H-1211							
H-1301							
CH_3Cl	1						
CH_3Br	**0.45**	1					
CH_3I	-0.27	-0.24	1				
CH_2Cl_2	**0.48**	0.19	0.03	1			
DCE	**0.51**	0.19	0.06	**0.71**	1		
MC	0.19	0.08	-0.11	0.05	-0.02	1	
CT	0.32	**0.45**	0.01	0.038	0.25	**0.44**	1

Table 5.6: *Correlation factors for some gases based of known episodes in European sector. Correlations better than 0.4 are showed in bold text. Numbers based on 2001-2003 data. Part 2*

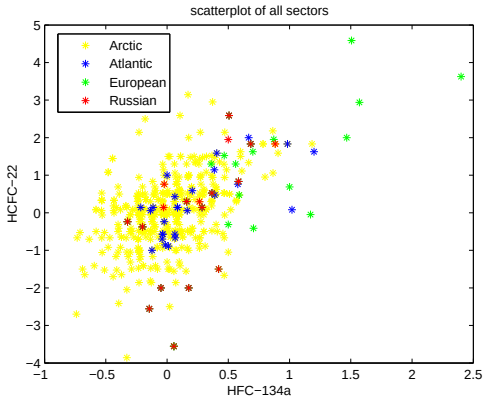
Compound .	**HFC 125**	**HFC 134a**	**HFC 152a**	**CFC 11**	**CFC 113**	**CFC 115**	**HCFC 22**	**HCFC 123**	**HCFC 124**	**HCFC 141b**	**HCFC 142b**	**H 1211**	**H 1301**
HFC-125	1												
HFC-134a	0.25	1											
HFC-152a	0.06	**0.47**	1										
CFC-11	-0.11	-0.06	0.19	1									
CFC-113	0.24	-0.09	0.18	0.27	1								
CFC-115	-0.16	-0.05	0.31	**0.45**	0.10	1							
HCFC-22	0.31	**0.60**	0.19	0.04	-0.21	0.21	1						
HCFC-123	0	-0.34	-0.15	0.29	0.23	0.29	0.11	1					
HCFC-124	**0.67**	.029	-0.18	-0.25	-0.11	-0.07	0.28	-0.01	1				
HCFC-141b	-0.03	0.05	0.37	**0.46**	0.38	**0.70**	0.05	0.08	0.13	1			
HCFC-142b	0.05	0.16	0.25	-0.18	0.02	**0.47**	0.27	0.10	**0.67**	0.23	1		
H-1211	0.13	0.38	0.32	0.33	**0.45**	0.35	0.20	0.10	-0.20	0.34	**0.43**	1	
H-1301	-0.22	0.14	-0.12	-0.19	-0.31	-0.14	0.07	**0.40**	-0.20	-0.26	-0.21	-0.17	1
CH_3Cl	-0.03	0.01	**0.40**	0.28	-0.04	-0.16	0.05	-0.04	0.02	0.16	-0.03	-0.14	-0.04
CH_3Br	0.10	0.39	**0.56**	0.05	0.25	0.01	0.31	-0.12	0.06	**0.41**	0.22	0.20	-0.24
CH_3I	-0.17	-0.41	-0.49	0.03	0.09	-0.14	-0.80	-0.20	-0.07	-0.10	-0.22	-0.12	-0.25
CH_2Cl_2	0.03	-0.05	0.34	-0.03	0.12	**0.51**	-0.24	-0.13	0.24	**0.53**	**0.48**	-0.09	-0.37
DCE	0.22	-0.25	0.15	0.27	**0.53**	0.06	-0.16	0.30	-0.22	-0.03	-0.37	0.08	-0.07
MC	0.12	0.18	0.04	**0.60**	**0.55**	-0.28	-0.28	0.22	-0.05	-0.03	-0.21	**0.42**	0.38
CT	0.11	0.24	**0.54**	-0.01	**0.63**	0.18	0.17	0.31	-0.26	0.29	0.26	**0.51**	-0.03

Table 5.7: *Correlation factors for some gases based of known episodes in Russian sector. Correlations better than 0.4 are showed in bold text. Numbers based on 2001-2003 data. Part 1*

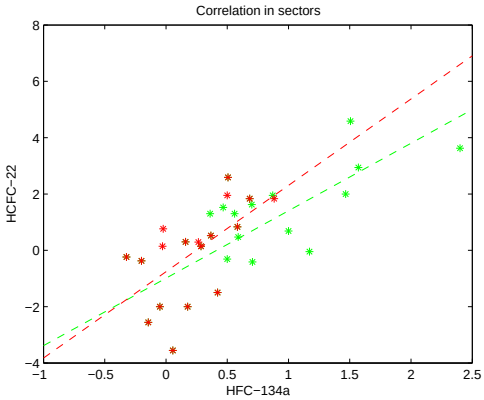
Compound	**CH_3Cl**	**CH_3Br**	**CH_3I**	**CH_2Cl_2**	**DCE**	**MC**	**CT**
HFC-125							
HFC-134a							
HFC-152a							
CFC-11							
CFC-113							
CFC-115							
HCFC-22							
HCFC-123							
HCFC-124							
HCFC-141b							
HCFC-142b							
H-1211							
H-1301							
CH_3Cl	1						
CH_3Br	**0.65**	1					
CH_3I	-0.21	-0.41	1				
CH_2Cl_2	0.14	0.23	0.15	1			
DCE	0.17	0.06	-0.03	-0.01	1		
MC	0.11	0.24	**0.46**	-0.49	0.02	1	
CT	0.04	**0.58**	-0.42	0.12	0.38	0.31	1

Table 5.8: *Correlation factors for some gases based of known episodes in Russian sector. Correlations better than 0.4 are showed in bold text. Numbers based on 2001-2003 data. Part 2*

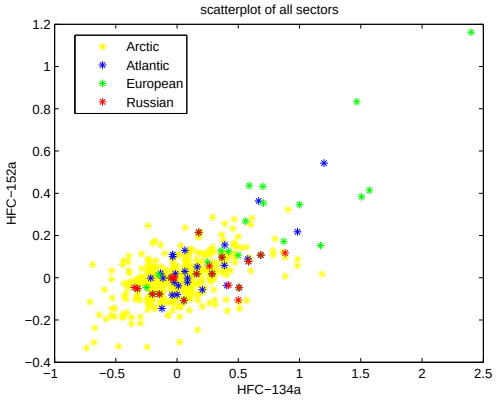
a) HFC-134a - HCFC-22, all sectors



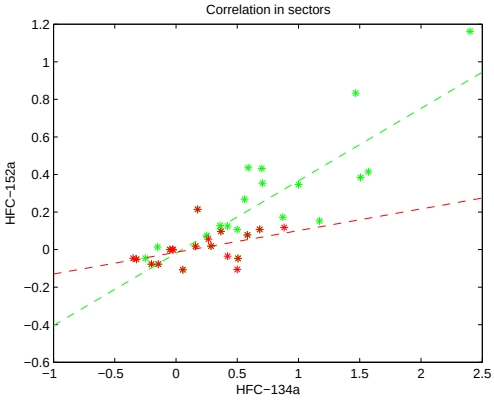
b) HFC-134a - HCFC-22



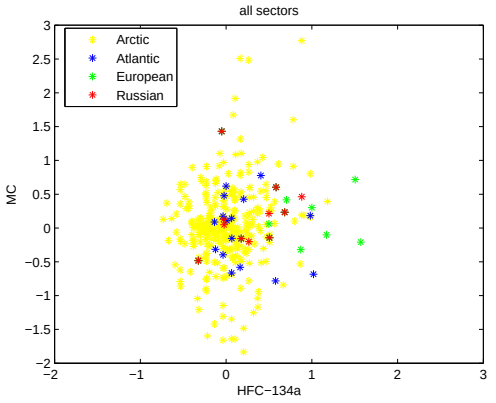
c) HFC-134a - HFC-152a, all sectors



d) HFC-134a - HFC-152a



HFC-134a - MC, all sectors



HFC-134a - MC

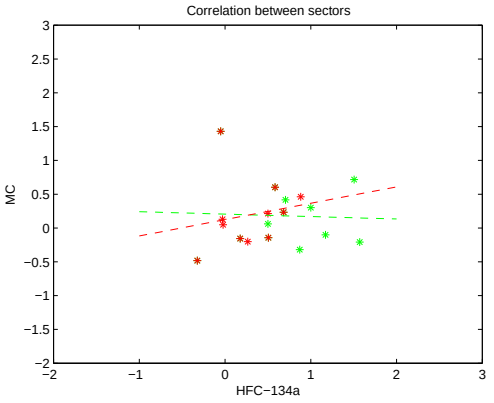
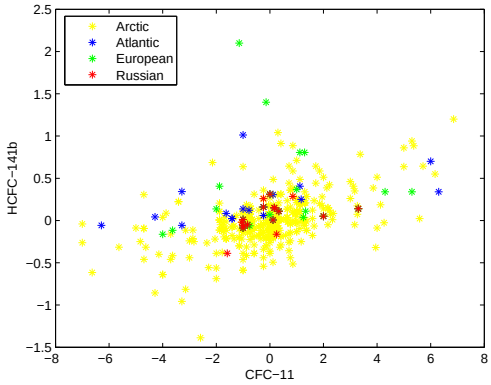
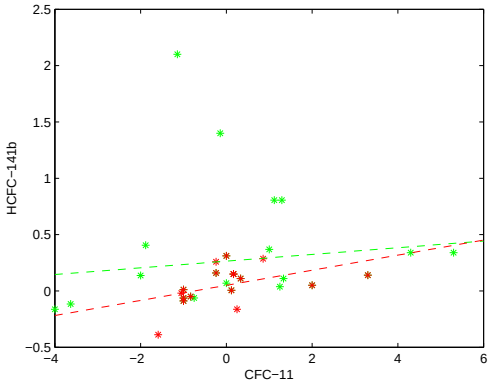


Figure 5.5: *Scatterplots of separated events. Both European and Russian sectors are shown. From the scatterplots of all values at the left hand side, we clearly see the European outliers denoted as green dots, visualizing the peak values in events.*

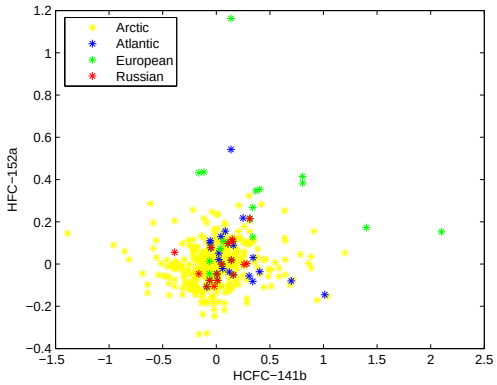
a) CFC-11 - HCFC-141b, all sectors



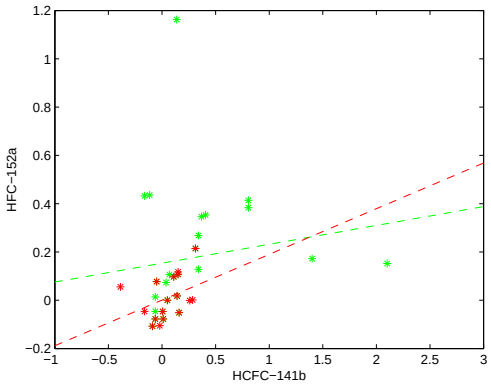
b) CFC-11 - HCFC-141b



c) HCFC-141b - HFC-152a, all sectors



d) HCFC-141b - HFC-152a



e) European emissions 2000 - 2003

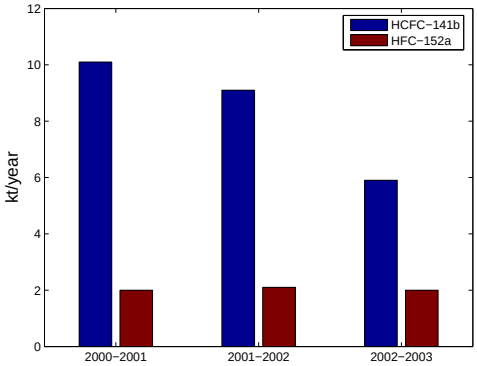


Figure 5.6: *Scatterplots of separated events for first generation (CFC-11 to HCFC-141b) and second generation (HFC-141b to HFC-152a) CFC-replacements. The outliers from the typical 'polluted' events are easily seen. European (green) and Russian (red) sector are shown separated in the left hand side plots. Estimated European emission source strengths (in kt/year) of HFC-141b and HFC-152a. [Manning et. al., 2003]*

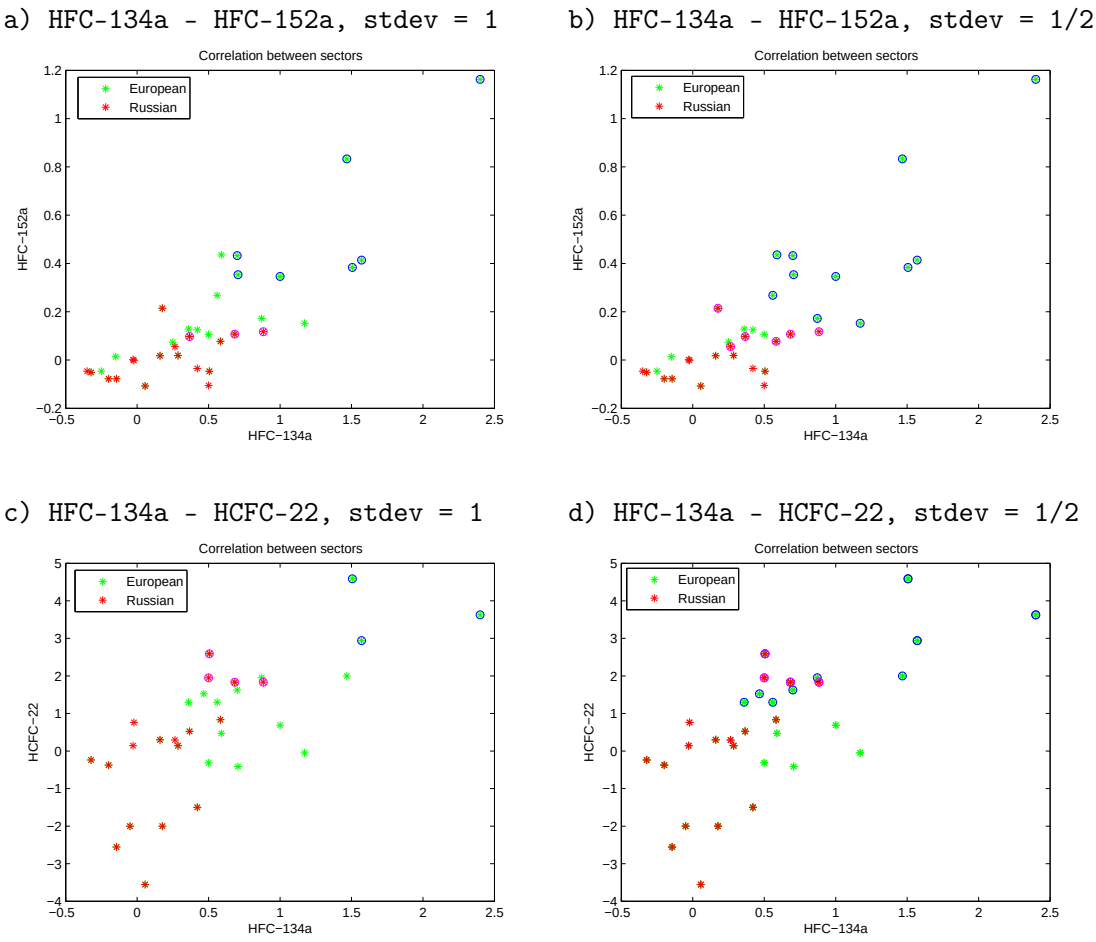


Figure 5.7: *Scatterplots of separated events, with different filters. Observation points marked with an 'o' denotes non filtered values. Only the peaks higher than 1, respective 1/2, standard deviation above the zero-line, not below, are passing the filter, to single out polluted events from the background. Both European and Russian sectors are shown.*

Chapter 6

Conclusion

In this paper we have studied the trends, seasonal cycles and the synoptic scale episodes of halocarbons observed at Ny-Ålesund. When comparing the 2001 - 2003 observations and the correlation coefficients at Mt. Zeppelin to the long term global trends, we find that the results presented here are in agreement with observations at other monitoring stations. The use of best fit polynominals is a well known method to estimate background trends. The distinct annual cycles in concentration due to either reaction with OH or seasonal differences in sources and/or global circulation can together with variations on longer timescales be described by a set of Legendre polynominals and harmonic functions.

The lifetimes, atmospheric trends and emissions of 20 compounds are investigated. The CFCs are about to level out and the first generation replacements, the HCFCs, are showing moderate increase in the atmospheric concentration. The second generation replacements, the HFCs, are still showing substantial yearly increase. HFC-134a and HFC-152a were estimated to have the greatest increase in the mixing ratios at Mt.Zeppelin in the 2001 - 2003 period, which is consistent with their high European emissions. The averaged seasonal cycles for some of the measured components are clearly showing a spring maximum and a summer or fall minimum. This yearly cycle is associated with the compounds predominant removal processing in the atmosphere and reactions with the OH radical and seasonality in other factors as mentioned above. Both Methyl Bromide and Methyl Chloride are unique among ozone-depleting halocarbons because a substantial fraction of their sources and sinks arises from biological processes. These processes may be affected significantly by changes in future climate. For the 3 year data set used in this document, we find that CH_3Cl and CH_3Br have positive trends, but the growth in the trends are decreasing. Growth rates, trends in the growth rates and seasonal amplitude factors for halocarbons at Mt. Zeppelin in 2001 - 2003 are listed in this thesis.

We have tried to estimate the location of regions in Europe and Russia which contribute to the observed elevated concentrations at Mt.Zeppelin. Thereby, the measurements were connected to respective back trajectories. Scandinavia, Great Britain and the European continent could be very potent

source regions for most of the halocarbons. This seems to be reasonable, especially northern Italy and Germany are heavy industrialized areas, where industries with known emissions of halocarbons are situated. For HFC-125 and HFC-134a Germany and the eastern part of France are potential source regions.

HCFC-22 and HCFC-141b consumptions have increased in the internal Russian market. Consumption of CFC-11 and CFC-113 was going down with production facilities closing in December 2000. There have been no CFC exports from Russia in the last four years. All these trends are seen in this work with the 2001 - 2003 SOGE data.

The internal correlations between the components have been investigated, to evaluate Russian and European source strengths. As an example, time series of HCFC-141b and HFC-152a are compared to the banned CFC-11. Due to its large historic production, the global CFC-11 concentration has accumulated to a level about 260 ppt and only recently shows a decay of 0.5% per year. The HCFC-141b levels are still increasing by about 1 ppt/year. Today the frequency and magnitude of pollution events form CFC-11 and HCFC-141b are nearly identical at most measuring sites. As mentioned in chapter 5, this is only to a lesser degree seen at Mt. Zeppelin. The events are few and small at this remote Arctic site.

Trends of each compound will be further investigated as the time series are expanded. The longer data record that is available, the more accurate the trend estimates will become. Future continuation of in situ GC-MS observations and subsequent quality control filtering should enable more reliable trend estimations.

Bibliography

Barrie, L. A., and R. M. Hoff (1985), Five years of air chemistry observation in the Canadian Arctic, Atmos. Environ., 19, 19952010.

Gentner, H., (1998), RACE (Refrigeration and Automotive Climate Systems under Environmental Aspects)

IPCC, 1996, Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories Guidelines

Madronich, S., G.J.M. Velders, J.S. Daniel, M. Lal, A. McCulloch, and H. Slaper (1999), Halocarbon scenarios for the future ozone layer and related consequences, in Scientific Assessment of Ozone Depletion: 1998, Global Ozone Research and Monit. Proj.–Rep. 44, pp. 11.1- 11.36, World Meteorol. Org., Geneva.

McCulloch, A., and P.M. Midgley (2001), The history of methyl chloroform emissions: 1951-2000, Atmos. Environ., 35, 5311-5319.

Midgley, P.M., and A. McCulloch, (1999), Properties and applications of industrial halocarbons. In Reactive Halogen Compounds in the Atmosphere. The Handbook of Environmental Chemistry.

Molina J. M., Rowland F. S. (1974), Stratospheric Sink for Chlorofluoromethanes: Chlorine Atom Catalysed Destruction of Ozone, Nature, Vol. 249, pp 810-812.

Montzka, S.A., J.H. Butler, J.W. Elkins, T.M. Thompson, A.D. Clarke, and L.T. Lock (1999), Present and future trends in the atmospheric burden of ozone-depleting halogens, Nature, 398, 690-694.

Montzka, S. A., C. M. Spivakovsky, J. H. Butler, J. W. Elkins, L. T. Lock, and D. J. Mondeel (2000), New observational constraints for atmospheric hydroxyl on global and hemispheric scales, Science, 288(5465), 500 503.

Montzka, S.A., P.J. Fraser, J.H. Butler, P.S. Connell, D.M. Cunnold, J.S. Daniel, R.G. Derwent, S. Lal, A. McCulloch, D.E. Oram, C.E. Reeves, E. Sanhueza, L.P. Steele, G.J.M. Velders, R.F. Weiss, and R.J. Zander (2003b), Controlled substances and other source gases,

in Scientific Assessment of Ozone Depletion: 2002, Global Ozone Research and Monit. Proj.–Rep. 47, pp, 1.1-1.71, World Meteorol. Org., Geneva.

O'Doherty, S., D.M. Cunnold, A. Manning, B.R. Miller, R.H.J. Wang, P.B. Krummel, P.J. Fraser, P.G. Simmonds, A. McCulloch, R.F. Weiss, P. Salameh, L.W. Porter, R.G. Prinn, J. Huang, G. Sturrock, D. Ryall, R.G. Derwent and S.A. Montzka (2004), Rapid growth of hydrofluorocarbon 134a and hydrochlorofluorocarbons 141b, 142b, and 22 from Advanced Global Atmospheric Gases Experiment (AGAGE) observations at Cape Grim, Tasmania, and Mace Head, Ireland, J. Geophys. Res., 109, D06310, doi:10.1029/2003JD004277.

Prinn, R.G., R.F. Weiss, P.J. Fraser, P.G. Simmonds, D.M. Cunnold, F.N. Alyea, S. O'Doherty, P. Salameh, B.R. Miller, J. Huang, R. H.J. Wang, D.E. Hartley, C. Harth, L.P. Steele, G. Sturrock, P.M. Midgley, and A. McCulloch (2000), A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, J. Geophys. Res., 105, 17751-17792.

Rhew, R. C., Miller, B. R., and Weiss, R. F. (2000), Natural methyl bromide and methyl chloride emissions from coastal salt marshes, Nature 403, 292295.

Rudolph, J., K. von Czapiewski, and R. Koppmann (2000), Emissions of methyl chloroform (CH3CCl3) from bio mass burning and the tropospheric methyl chloroform budget, Geophys. Res. Lett., 27, 1887-1890.

SFT. (1993), Greenhouse gas monitoring at the Zeppelin station. Annual report.

Stohl et. al., (1995), Air mass trajectories from the FLEXTRA trajectory model, calculatoions from S.Solberg, NILU (2004)

UNEP (United Nations Environment Programme), Production and Consumption of Ozone Depleting Substances under the Montreal Protocol 1986-2000, Ozone Secretariat, Nairobi, Kenya (see www.unep.org/ozone), 2002.

Waggoner, M., H. D. Ohr, C. Adams, J. J. Sims, and D. Gonzalez, Methyl iodide (2000), An alternative to methyl bromide for insectary fumigation, J. Appl. Entomol., 124, 113117.